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FINAL REPORT
FEASIBILITY PROOF OF DRY TAPE
BATTERY CONCEPT

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ABSTRACT

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Feasibility of the "Dry Tape Battery" concept has been demonstrated using the divalent silver oxide (Ag_2O_2)-zinc couple with potassium hydroxide electrolyte. Tapes coated with Ag_2O_2 have been discharged efficiently (85%) at high current density (150 amp/ft^2) against a zinc block anode in a demonstration device. Methods of making and activating Ag_2O_2 tapes have been devised. Tape speed, electrolyte feed rate, and other operating parameters have been investigated and evaluated as necessary for the design of a demonstration device. Four such devices were constructed and delivered with sufficient tape decks for several hours of operation.

Additional investigations carried on from 19 December to 23 January 1964 are reported in Appendix II.

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I. INTRODUCTION

A. OBJECTIVE

The major objective of this work was to demonstrate the feasibility of the "dry tape" concept by constructing a breadboard device to use experimentally coated tapes based on the Ag_2O_2/Zn couple. In addition, the operating parameters of this experimental system were to be determined so that reasonable extrapolations of system capability for larger systems and other electrochemical couples could be made.

B. BACKGROUND

The "dry tape" concept in its ultimate form involves the use of a thin separator tape on which are coated the active components of an electrochemical system (oxidant, reductant, electrolyte, electrode, etc.). This tape can then be fed continuously or intermittently to a set of current collectors that would activate the system, allowing the electrochemical reactions to take place.

The major distinction between primary batteries and fuel cells is a matter of system invariance. A primary cell is completely self-contained; during operation, fuel and depolarizer are depleted while waste reaction products accumulate. In a fuel cell, a more invariant system is provided by continuous feeding of reactants and withdrawal of products. This system is still not completely invariant, however, since separators degrade, catalysts become poisoned, and electrodes can flood. Furthermore, mass transport or diffusional processes often limit the operation of both batteries and fuel cells, although generally this problem is more severe with batteries than it is with fuel cells.

The dry tape concept is designed to minimize, if not eliminate, some of these common failings of both batteries and fuel cells. It is a step towards more complete system invariance because not only the fuel and oxidant but also the separator, electrodes, catalyst, and electrolyte are fed unused into the system.

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The major advantages visualized for such a system are, first, reduction of concentration and activation polarization through continuous feed of reactant and removal of products and the continuous feed of fresh electrode surface. Second, such a system would allow the use of known, high energy couples in high rate applications, whereas in conventional battery systems these same couples would be limited to low rate applications because of mass transport limitations. A third advantage of the dry tape concept is that with reserve-type materials, activation of components would occur only as they are needed, permitting unlimited storage of the unactivated portion of the tape.

The complete development of such a system would require a total effort that would not be justified until the feasibility of the basic concept is demonstrated. For this reason, our major effort has been to demonstrate the feasibility of the concept in a very elementary form. Electrolyte incapsulation, catalysts, etc., were not considered in this initial program. For demonstration purposes, the Ag_2O_2/Zn couple was used for comparison with other high rate battery systems. The program was not designed necessarily to optimize this particular couple but rather to demonstrate its feasibility by determining the operating parameters so that sound extrapolations to future system capability can be made.

II. SUMMARY AND CONCLUSIONS

The feasibility of the "Dry Tape Battery" concept has been shown with the Ag_2O_2/KOH/Zn system. A cathode (Ag_2O_2) utilization of 85% was attained at high current density (150 amp/ft²), while at lower current densities cathode utilization approached 100%.

The cathode material, Ag_2O_2, was applied in aqueous slurry with a binder to a nonwoven fabric base to form a flexible tape. Discharge was accomplished by drawing the tape between the current collectors, one of which also served as the zinc anode. Electrolyte was supplied by a second tape, prewet, which contacted the coated tape prior to the current collectors.

Investigation of the various operating parameters of the tape system provided the following operating ranges:

Current Density	- up to 200 amp/ft²
Tape Speed	- 0.2 to 1.5 in./min
Electrode Contact Pressure	- 0.1 to 0.8 lb/in.²
Electrolyte Feed Rate	- 0.15 to 0.3 cc/min

Using the above operating ranges, a demonstration device was designed and four such units were constructed. These units were delivered with 20 tape decks sufficient for several hours of operation. The demonstration units were not weight optimized but designed to show feasilibilty of the concept for application to systems of theoretically high energy density.

It is concluded that the "Dry Tape" concept is feasible and that it can be used to improve the high-rate discharge characteristics of high energy density couples. The power required to drive the tape system is small compared to the output power. Relatively incompatible couples can be used since it has been shown that activation can be accomplished just prior to discharge.

III. PHASE IA. MECHANICAL ASPECTS

A. LABORATORY TAPE EVALUATION DEVICE

A laboratory test device for evaluation of experimental tapes was constructed before the formal start of the project. Figures 1 and 2 are photographs of this device as set up for "dual tape" operation. In dual tape operation, an uncoated tape wetted with electrolyte joins the coated tape just before entering the current collectors.

The dual tape is driven by a variable speed dc motor coupled to a reducing gearbox and a torque-measuring device. Initially, electrolyte was fed from a micrometer syringe (6), powered by a Zero-Max variable speed drive (7), to a wicking pad (5) to distribute the electrolyte onto the uncoated tape before it joins the coated tape. After a satisfactory range of electrolyte feed rates was determined by this method, the uncoated tape was pre-wet with the desired quantity of electrolyte to more closely simulate the operation of the breadboard demonstration units.

Figures 1 and 2 show the laboratory tape evaluation device set up for "dual-tape", syringe-feed electrolyte operation. The dry Ag_2O_2 coated tape (1) is pulled over a platform and then passed between stainless steel rollers (17), where it is pressed against the previously wetted electrolyte/separator tape (13). The separator tape is wetted as it passes over the electrolyte wicking pad (5). The wetted tape (15) is drawn with the separator between the current collectors (2), the lower one of which is a zinc block. The upper current collector, a silver plate mounted on Plexiglas Ⓡ, is positioned by the guide (14) and screws (18). The discharged tape (16) is drawn up on the tape-up spindle (3), which is driven through the torque meter (12).

1. Cathode Collector

The cathode collector was originally a flat silver strip under which the Ag_2O_2-coated tape passed. It was found that performance of tapes with rough coatings could be improved by use of a flexible grid of expanded silver as the current collectors. With somewhat smoother coatings, no noticeable improvement was found with expanded silver. The area of the cathode collector (and the coated tape width) was reduced to 0.765 in.^{2} (7/8 in. x 7/8 in.) to provide more reliable operation with the "dual-tape" system. The collector weighed approximately one ounce, and contact pressure was varied by the addition of one-ounce weights.

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KEY FOR FIGURES 1 AND 2

1 Dry tape, Ag_2O_2 coated

2 Current collectors

3 Tape take-up

4 Take-up drive and motor

5 Electrolyte wicking pad

6 Electrolyte pump (micrometer syringe)

7 Zero-Max pump drive, variable speed

8 Tape take-up speed control

9 Load box, 1 ohm steps

10 Dual pen recorder

11 Current shunt

12 Tape drive and torque meter

13 Separator tape, wet

14 Tape guide-cathode current collector guide

15 Wetted tape

16 Discharged tape

17 Contact rolls

18 Cathode current collector positioning screws
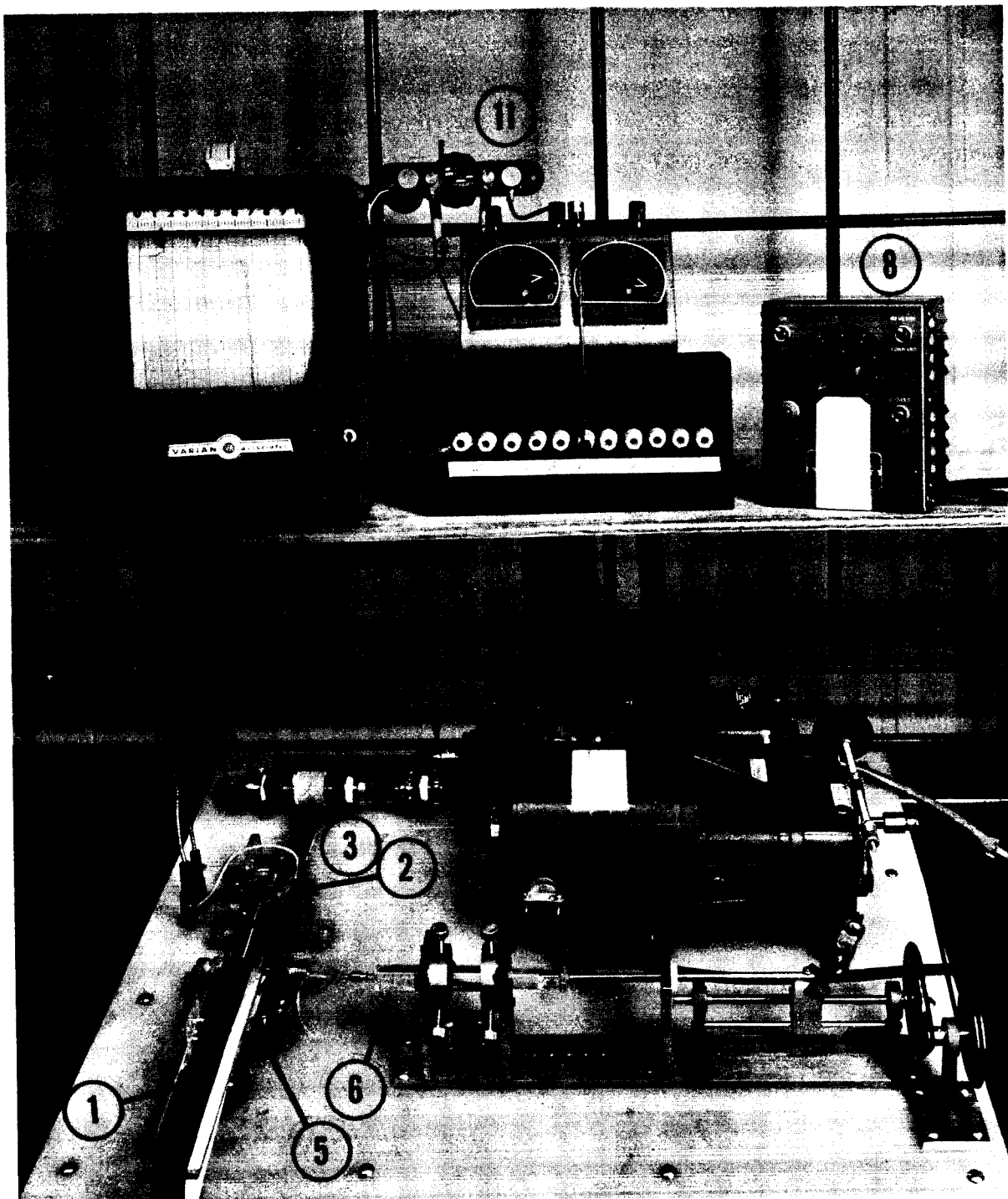
Figure 1. Laboratory Tape Dynamic Test Device
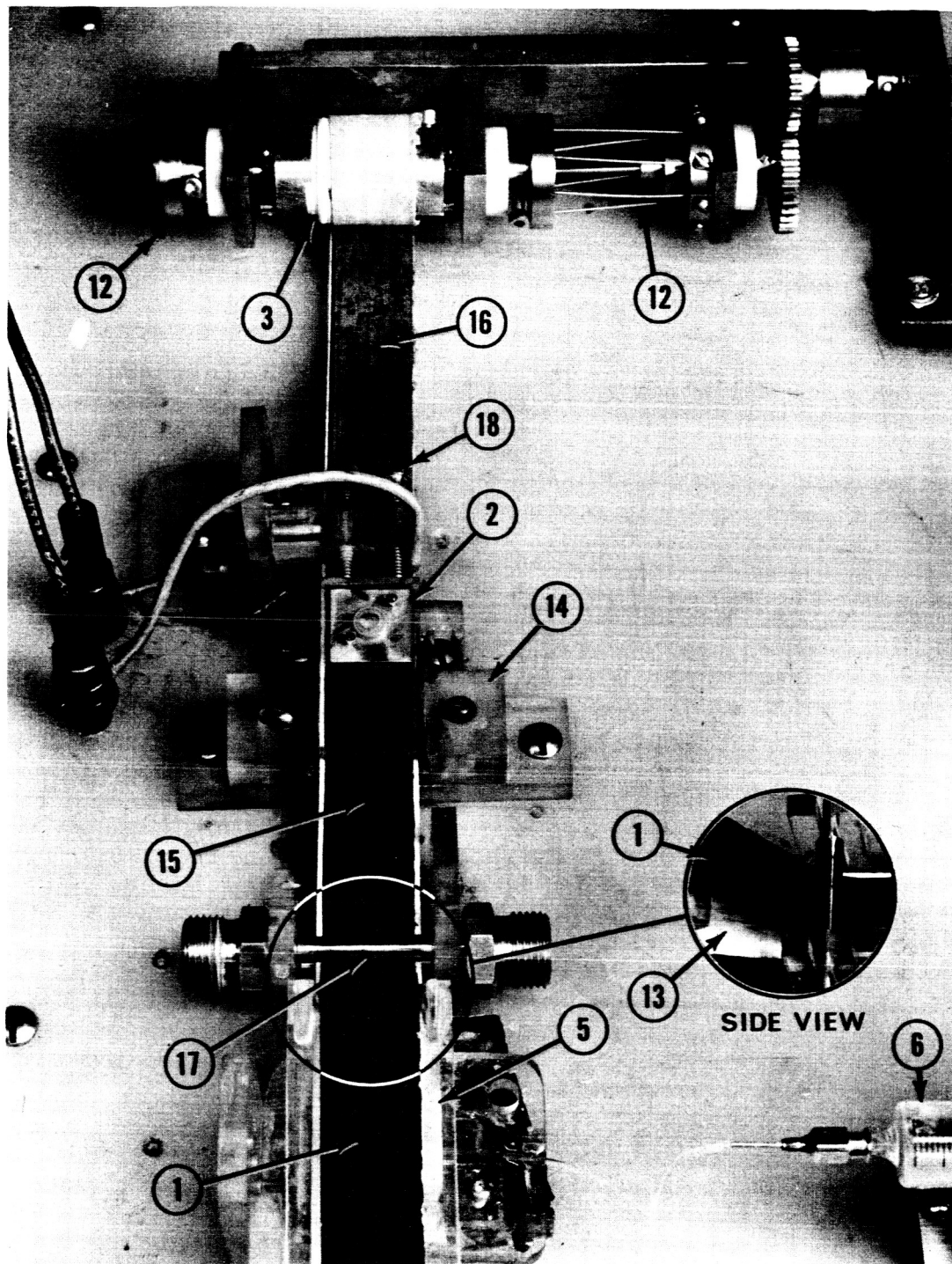
Figure 2. Tape Section of Dynamic Test Device -
Dual Tape Operation

As an alternative to the flat, sliding collector described above, a roller collector was built and tested briefly. The purpose of this was to reduce the force required to pull the tape. The roller collector consisted of four 1/8-in. diameter gold-plated rollers set in a holder. Preliminary tests indicated that the higher current densities encountered at the roller contact areas were tolerable.

2. Anode Collector

For this feasibility study, the zinc anode material was not coated on the opposite face of the tape but rather was present as a block over which the activated tape was drawn. The zinc block also served as the anode collector. The anode collector area was varied from 0.328 in.^{2} to 0.985 in.^{2} by varying the collector length from 3/8 in. to 1 1/8 in. with a fixed width of 7/8 in. Expanded zinc screen was also tried as the anode collector. The screen was consumed in a relatively short period of operation and no improvement in performance was noted.

3. Discharge Circuitry

The electrical load consisted of a resistance box with ten 1-ohm (25 w) resistors connected in series and tapped at 1-ohm steps. These resistors and the circuit resistance were measured with an Electro Scientific Industries Universal Impedance Bridge. The 1-ohm resistors (connected) were found to be within 2% of that value, and the circuit resistance was approximately 0.075 ohm (excluding electrodes) of which 0.05 ohm could be attributed to the current shunt. Electrical output was measured with a Varian G-22 Dual Channel Recorder, which provided a continuous record of current and voltage. Full-scale voltage was 2 volts, and 1- and 2-amp (full scale) shunts were generally used. Accuracy was 2% of full scale and better. A chart speed of 2 in./min was used most often to give a convenient and accurate comparison with tape speed (usually 1 in./min).

B. DESIGN AND CONSTRUCTION OF BREADBOARD DEMONSTRATION DEVICE

To demonstrate the feasibility of the dry tape concept, breadboard hardware was designed and constructed. Because of time limitations, certain design considerations were initially agreed upon. These were:

a. The unit was to be completely self-contained (drive, tape, electrolyte, etc.).

b. A spring-wound mechanism (off-the-shelf) was to be used for tape transport.

c. A zinc block, over which the Ag_2O_2 tape is passed, was to serve as the anode rather than using a zinc coating on the tape.

d. Commercially available Ag_2O_2 was to be used directly as the cathode material rather than use of in situ electrolytic formation.

e. The configuration of the components in the breadborad units was to occupy as small a volume and be as light as possible consistent with using "off-the-shelf" parts wherever possible.

f. The breadboard demonstration device was to be capable of continuous operation for at least 10 minutes, limited only by the length of tape, even though the mechanical system capacity would be much higher.

g. Although the ultimate goal was to use electrolyte encapsulation, for demonstration purposes this was not to be done.

As work progressed, a further constraint was put on the demonstration device. It was felt that for the short periods of operation required for demonstration, a weight and time saving and more reliable operation could be obtained by using a dual-tape system in which the electrolyte would be fed on a second tape saturated with aqueous KOH. This greatly simplified the supplying of electrolyte.

1. Component Design and Testing

To check out possible mechanical designs for the breadboard demonstration devices, it was necessary to construct a test stand in which the mechanical features of all proposed components could be determined individually and in conjunction with one another. This test stand is shown in Figure 3. Based on their performance in this test stand, the design of the various components was frozen for imcorporation into the final devices.

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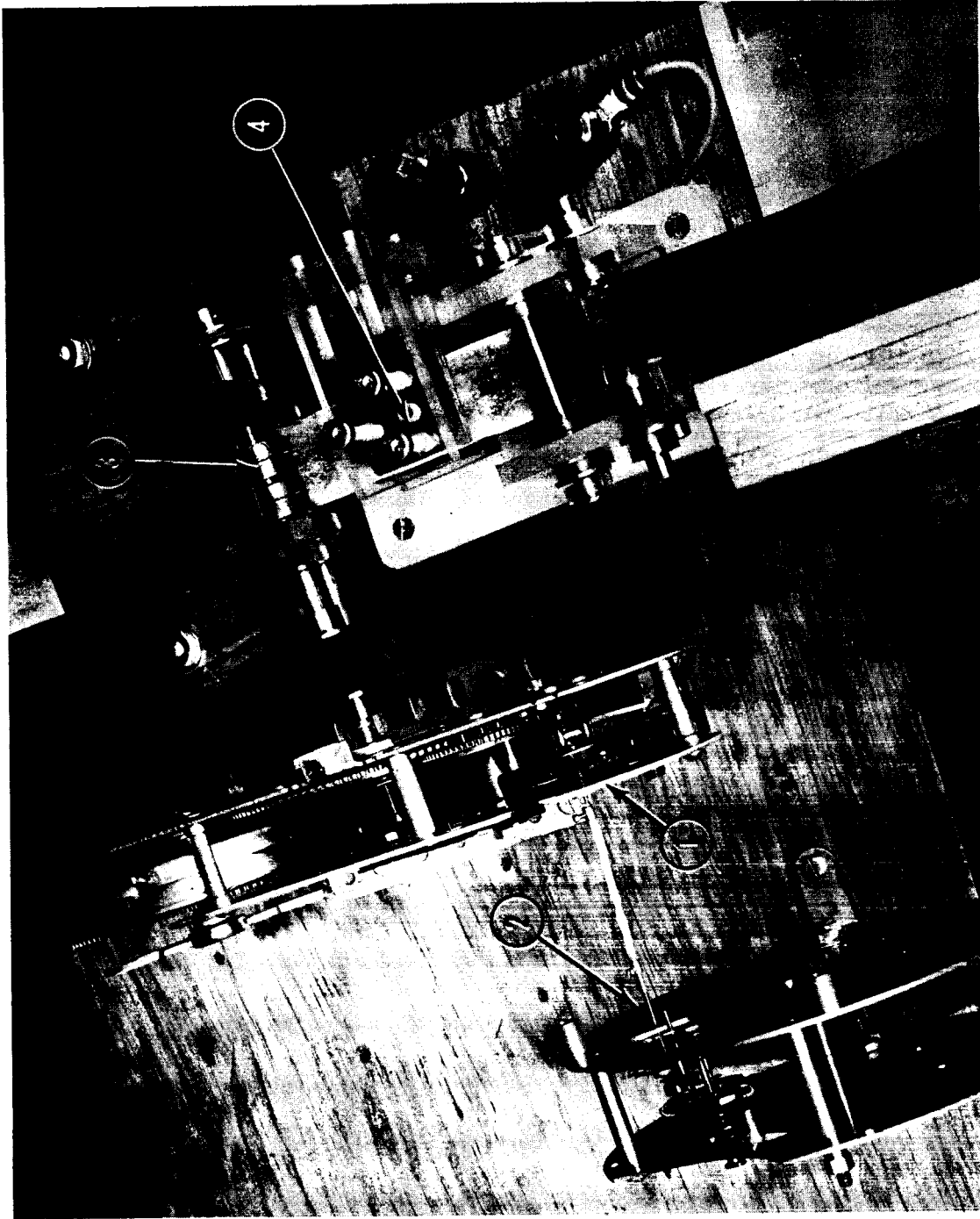
1. Spring-wound drive (Keystone A-7-3)
   with disengaged centrifugal governor
2. Attached escapement mechansim

3. Tape transfer drive
4. Current collectors

Figure 3. Component Test Stand – Top View
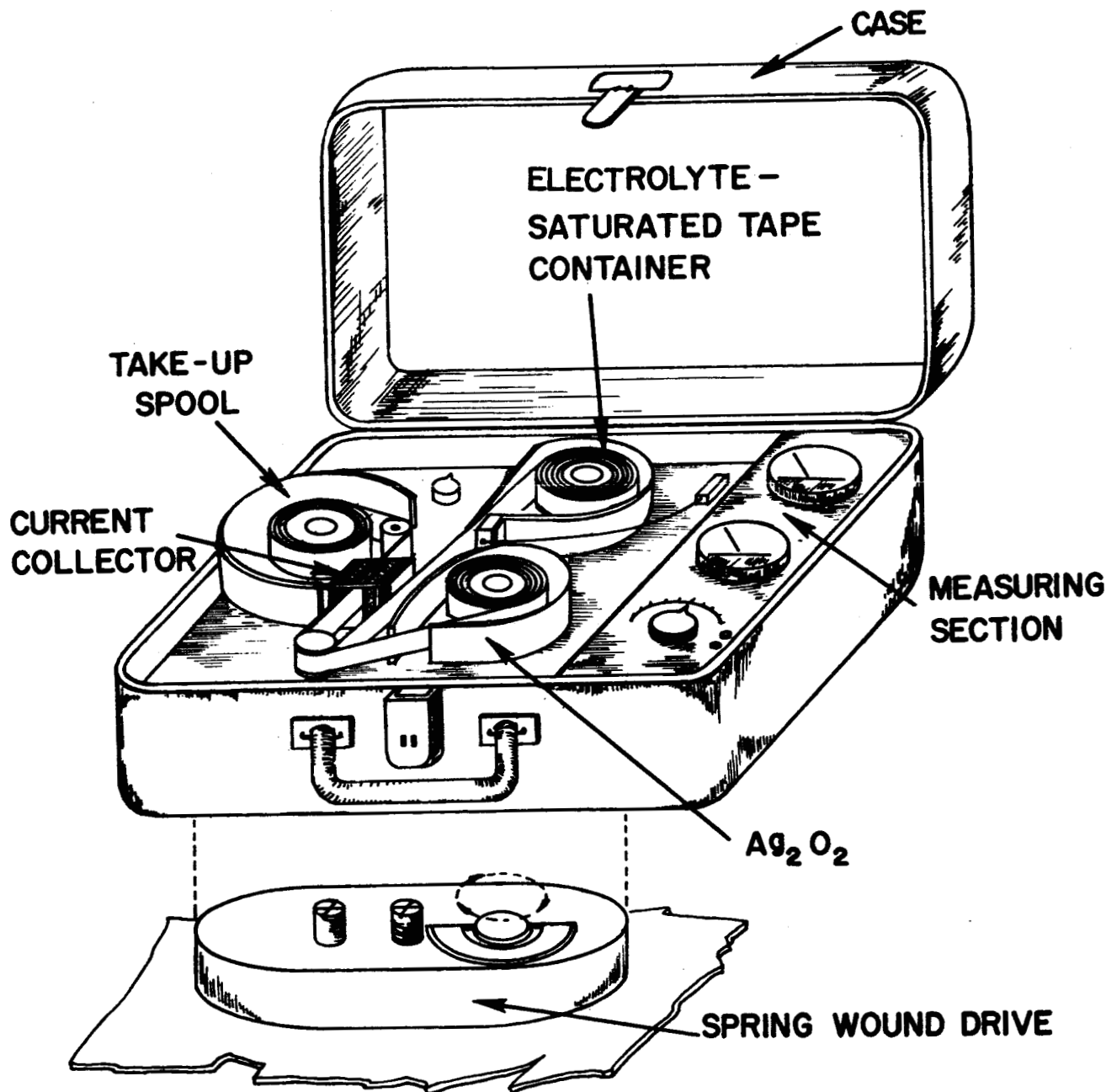
Figure 4. Prototype Demonstration Model of Dry Tape Battery

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It is interesting to note that the electrical output of a tape
tested in this rig was identical with that obtained in the tape
evaluation device.

2. Breadboard Demonstration Device: Design and Fabrication

   a. General Description of the Prototype Model

Basically, the breadboard units that were delivered consisted of
two major sections. The first contained a spring-wound drive
permanently mounted in a carrying case. Also mounted in this
case was a variable load resistor, a voltmeter and an ammeter
for demonstration purposes.

The second section, which is called the "tape deck", is a self-
contained unit comprising the Ag_2O_2 tape spool, electrolyte
saturated tape spool, tape sprocket drive wheel, and current
collectors. Tape decks were built with sufficient tape for
approximately 25 minutes of continuous operation and can be
"plugged into" any drive unit.

A pictorial view of the breadboard unit is shown in Figure 4.
Figure 5 is a plan view of the tape deck in which the various
components are mounted.

The tape spools were preloaded with Ag_2O_2 and electrolyte-saturated
tape. Non-permeable leaders made of polyvinylchloride were
attached to the tapes and threaded through the operating path.
This preloading was done during the actual fabrication of the tape
deck, not just prior to the use of it. To start the unit, a tape
deck was plugged into the carrying case, over the spring-wound
motor section. The process of "plugging in" automatically en-
gage the tape drive sprocket wheel and take-up spool shafts to the
spring motor shaft through self-sligning couplings.

Before actually starting the unit, the seal from the electrolyte
tape container had to be removed and the tape advanced manually until
the active coated tape was within the current collectors. Turning
the starting knob connected to the spring wound motor there put
the unit into operation.

Details of the individual components of both the drive unit and
the tape deck are discussed in the following section.

   b. Detailed Component Description

      (1) Spring-Wound Motor
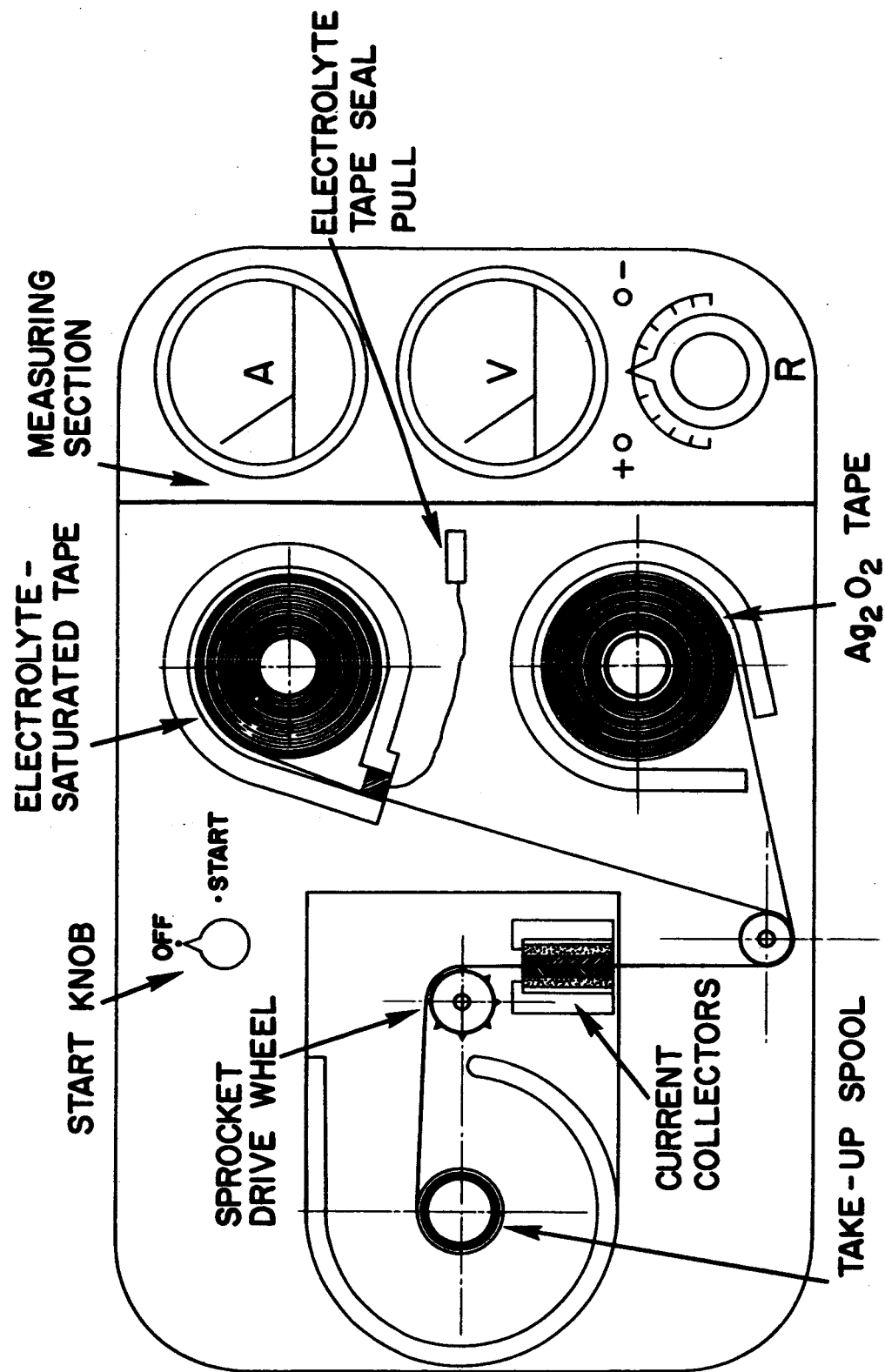
Figure 5. Tape Deck Assembly of Prototype Demonstration Battery

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It was decided at the start of this project, that for the sake of simplicity, a spring-wound motor would be used to drive the tape system. Previous experiments had shown that the drive should be able to provide a shaft output of 10-12 in.-oz of torque at 0.568 rpm. A further requirement was that the spring-wound motor should run at least 20 minutes at constant speed after a complete winding.

Because of the tight schedule for this work, it was necessary where-ever possible to select off-the-shelf components rather than to design them individually. For this reason, it was necessary to take a weight penalty in obtaining a commercially available spring-wound motor that would do the job. It was found that the drive mechanism of a 16 mm Keystone movie camera (No. A-7-3) with the following specifications would be satisfactory with modification:

Output shaft speed:	60 rpm minimum
Output shaft torque:	20 in.-lb when fully wound
Max. running time:	65 sec
Take-up spool shaft speed:	60 rpm minimum
Take-up spool shaft torque:	approx. 0.5 in.-lb
Weight:	2.3 lb

The original speed control of the camera drive was insufficient to reduce the output shaft speed to 0.568 rpm. For this reason an escapement mechanism from a chart drive clock was connected to the camera drive in place of centrifugal regulator originally supplied. The general layout of this modified spring-wound drive is shown in Figure 6. The transplanted escapement mechanism incorporated into the original Keystone drive unit is in the left-hand portion of Figure 6.

To rotate the tape deck shafts, a flexible coupling arm was mounted on the take-up spool and tape drive shafts. When the tape deck was "plugged in", these flexible coupling arms engaged jawed couplings on the tape deck shafts, providing a very satisfactory flexible shaft connection.

(2) Tape Transfer Drive

The threaded tape within the tape deck was pulled along its operating path between the current collectors by a drive wheel that has two sets of sharp sprocket teeth as shown in Figure 7 and 8. Thus, the tape was transfered by the progressive motion of the penetrating

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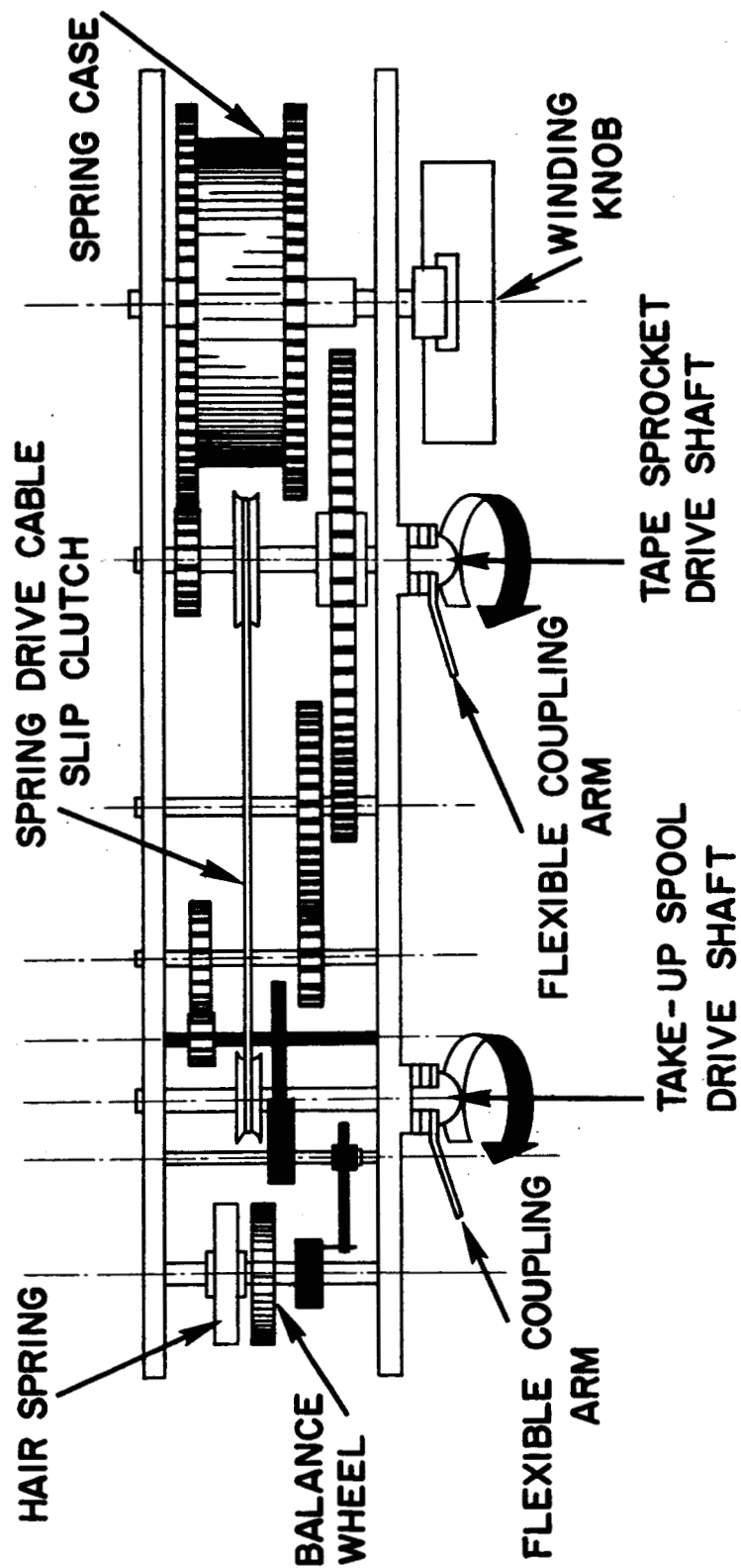
Figure 6. Spring-Wound Drive Unit - Top View

SPRING CASE

WINDING KNOB

SPRING DRIVE CABLE
SLIP CLUTCH

FLEXIBLE COUPLING
ARM

TAPE SPROCKET
DRIVE SHAFT

TAKE-UP SPOOL
DRIVE SHAFT

HAIR SPRING

BALANCE
WHEEL

FLEXIBLE COUPLING
ARM

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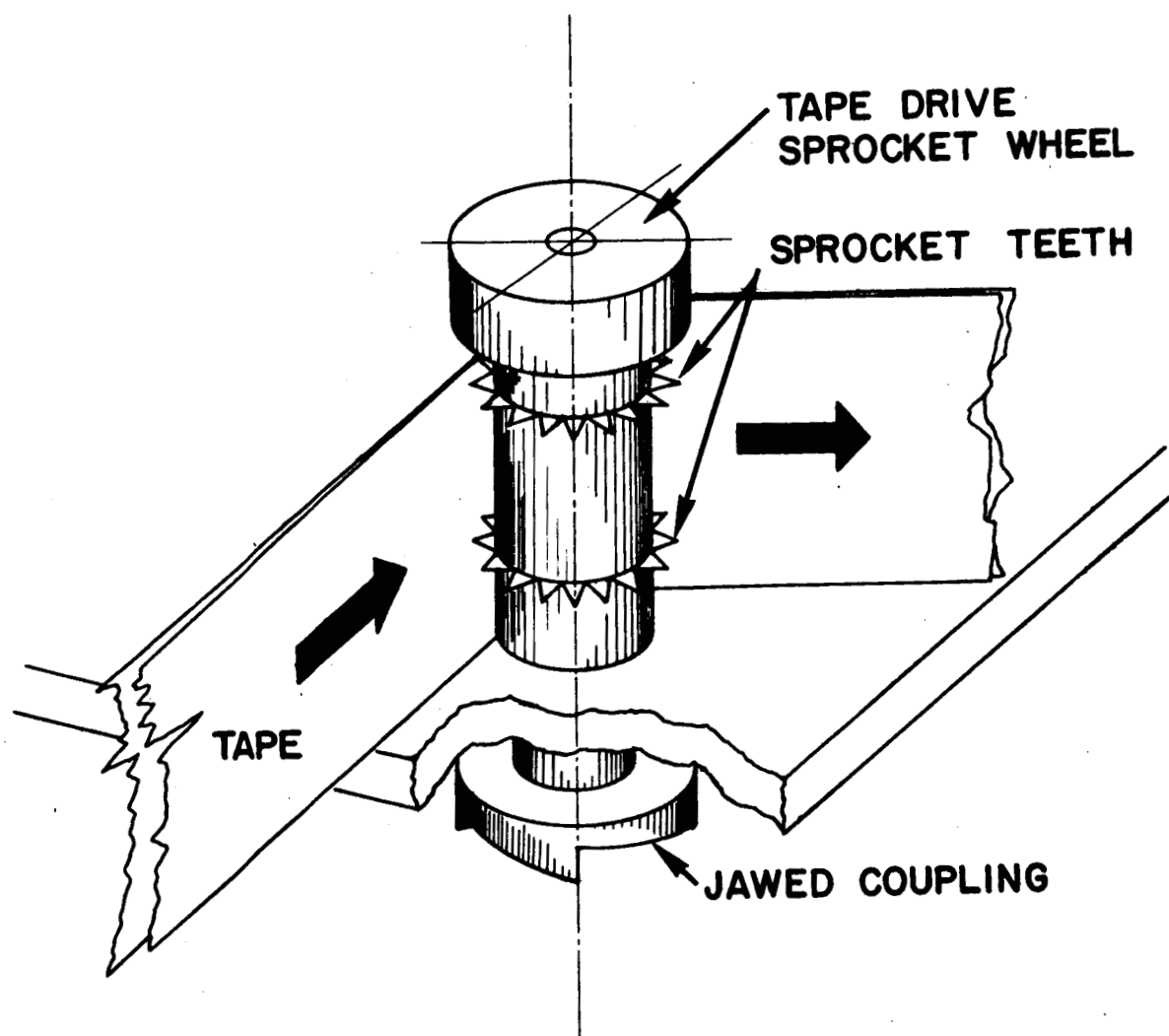
Figure 7. Tape Transfer Drive
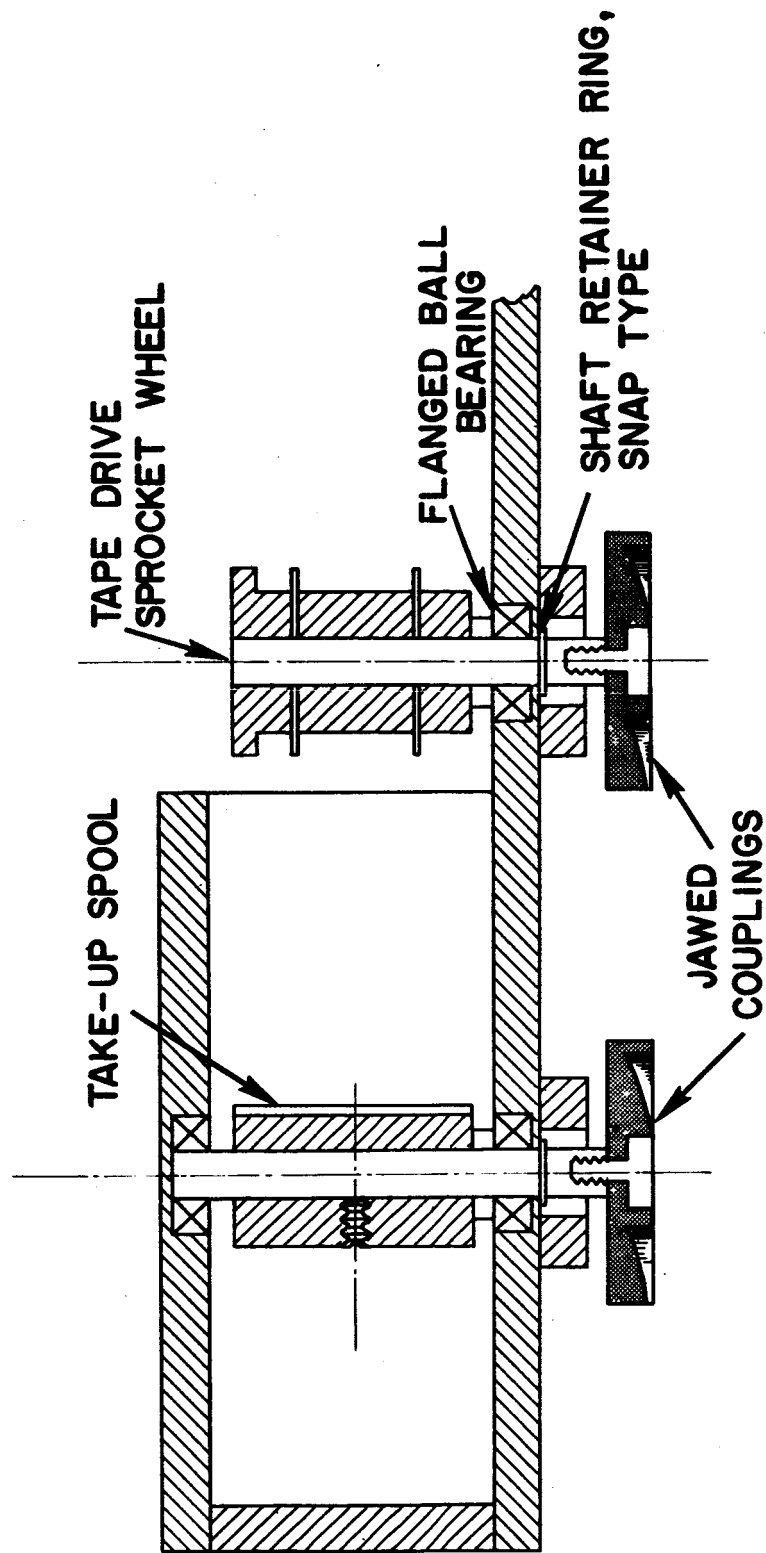
Figure 8. Cross-Section of Tape Transfer Drive and Takeup Spool

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sprocket teeth. The optimum shape and dimensions of sprocket teeth that would operate equally well on all combinations and thicknesses of tapes and separators was not developed, but good traction characteristics were obtained with triangular-shaped 5-mil thick stainless steel teeth.

Mounted on the driven end of the tape drive sprocket wheel shaft, as shown in Figures 7 and 8, was a jawed coupling. When the tape deck was plugged in, the flexible arms on the spring motor drive shafts engaged the jawed couplings on the drive shafts. At a shaft speed of 0.568 rpm, the tape was driven at a linear rate of about 1 inch per minute.

(3) Take-Up Spool Drive

As shown in Figure 8, the take-up spool shaft was driven in the same manner as the tape drive sprocket shaft. The major difference was that only sufficient torque was provided the take-up spool shaft to overcome friction and wind the tape on the spool. Since the rate of rotation of the take-up spool decreases as spent tape is wound on the spool, a slip clutch was used in the spring motor between the tape drive sprocket shaft and the tape-up spool shaft. The slip clutch was a spring drive cable as shown in Figure 6, which merely slipped on the pulleys because of the speed differential.

(4) Current Collectors

The current collectors, shown in Figure 9, were designed to fulfill the following requirements:

(1) Even contact pressure over the moving tape and the stationary anode.

(2) Knee-action to follow small unevennesses of the tape.

(3) Simple assembly and disassembly.

One of the two current collectors was made of fine silver and served as the cathode collector. The other consisted of a zinc block and served as both current collector and anode. Each of the elements was of sandwich structure and consisted of the current collector metal bonded to 1/4-in. thick urethane sponge, which in turn was bonded to a Plexiglass ® backing plate. The total width of the electrode casing was selected to give approximately 6 oz/in.^{2} of pressure between the current collectors.

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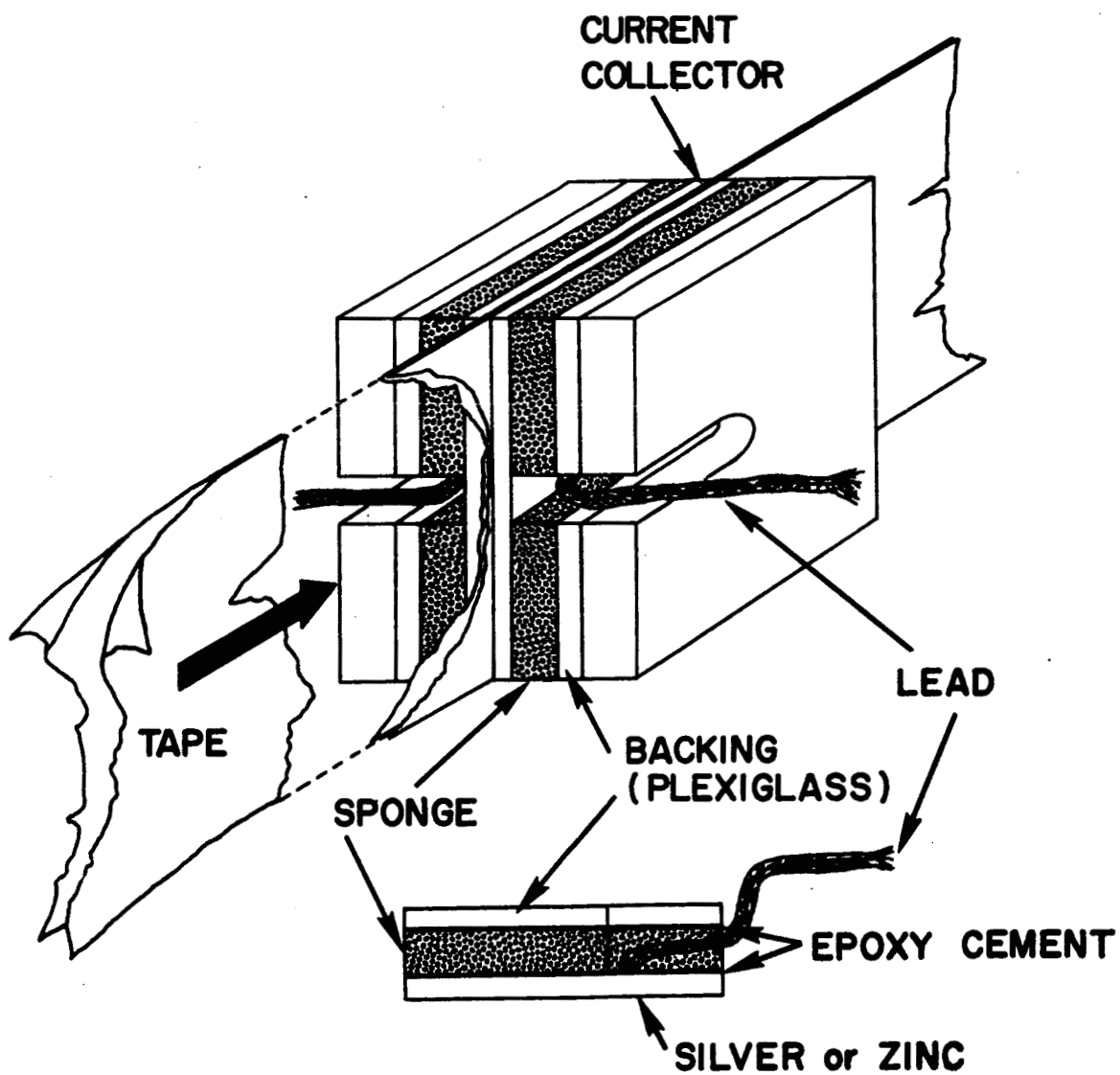
Figure 9. Current Collector Assembly

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(5) Electrolyte Tape Container

Since in the dual tape system an electrolyte-saturated tape is stored on a separate spool, it was necessary to seal this container in some manner to prevent loss of electrolyte through evaporation. The seal was made as shown in Figure 10. A soft neoprene rubber cylinder of 12 durometer hardness was compressed into the lip opening of the container against the nonpermeable section of the tape leader. The seal was removed manually just prior to use of the tape deck.

To determine the effectiveness of this seal, one container was sealed with 30% KOH-wetted tape on 19 November 1963. On 2 December 1963 this container was opened briefly and the tape was found to be still wet. This container was resealed and put in storage. On 2 January 1964 the container was checked again (without opening) and still appeared satisfactory; at no time was any "frosting" noted on the seal or container.

ELECTROLYTE
SATURATED TAPE

STITCHING

FINGER GRIP
SEAL REMOVER

TAPE LEADER

RUBBER CORD
SEAL
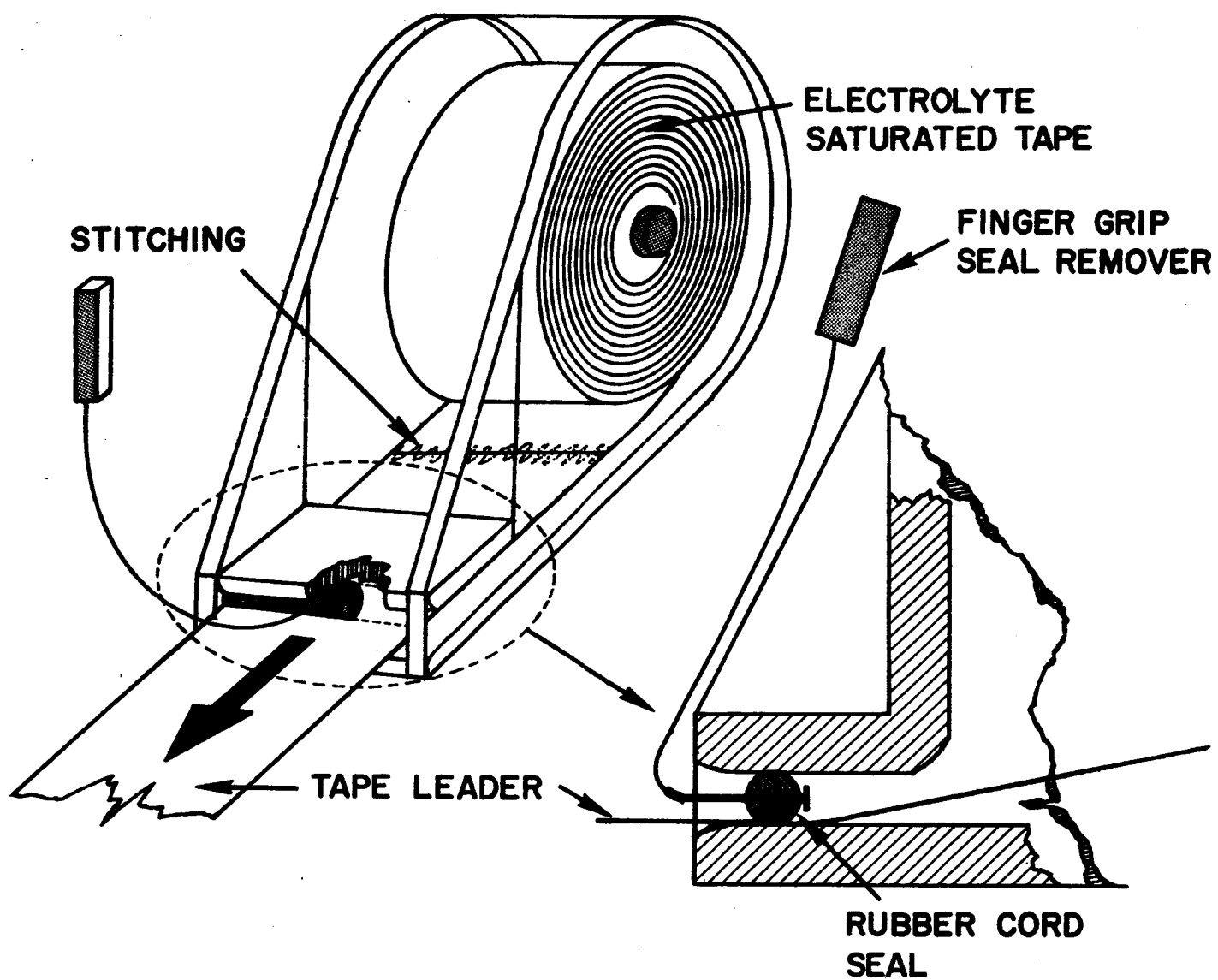
Figure 10.   Electrolyte Tape and Container

IV. PHASE IB. CHEMICAL ASPECTS

A. ELECTROCHEMICAL SYSTEM

The Ag_2O_2-Zn system was used in this work to allow comparison
with a known battery system capable of high discharge rates. The
electrochemical equivalents for this system are listed below. The
quantity of electrolyte required depends upon which reaction
predominates: 1a, 1b, or 1c.

			Theoretical Energy Density Watt-hr per lb reactants	
			As Written	Using 30% KOH
(1a)	$Ag_2O_2 + 2Zn + 2H_2O = 2Zn(OH)_2 + 2Ag$		176	169
(1b)	$Ag_2O_2 + 2Zn + 2KOH = 2KHZnO_2 + 2Ag$		149	97
(1c)	$Ag_2O_2 + 2Zn + 4KOH = 2K_2ZnO_2 + 2H_2O + 2Ag$		121	65

The theoretical energy density listed with each reaction assumes com-
plete discharge at 1.5 volts and was calculated using the following
electrochemical equivalents:

		g/amp-hr
	Ag_2O_2	2.305
	Zn	1.220
Reaction (1a)	H_2O	0.335
Reaction (1b)	KOH	1.045
Reaction (1c)	KOH	2.090

For a number of reasons, the theoretical energy density cannot be
realized. Some zinc (5 to 10%) chemically dissolves in the electrolyte
and therefore is not used electrochemically. Internal resistance
of the cell and the need for some excess electrolyte are among other
factors lowering the energy density obtained.

B. TAPE FABRICATION

Production of a suitable coated tape involved selection of a base
material, binder, and coating method for applying active divalent
silver oxide cathode material to the base in a form suitable for
discharge.

1. Anode

As mentioned previously, the anode consisted of a zinc block over which the activated tape was drawn. A zinc-coated tape anode was also made by dispersing zinc powder in a polyvinyl alcohol-water solution and drawing the resulting slurry over a strip of Gelman PVA separator with a Gardner knife. The coating was physically satisfactory, showing good flexibility, uniformity, and rub-resistance. This tape was not characterized electrochemically, however.

2. Tape Base Materials

It was not intended to make an exhaustive study to select the best base material, but rather to find, as quickly as possible, a satisfactory tape for use in the demonstration devices. This was necessary to facilitate design of the tape drive and associated hardware.

Nonwoven fabrics of Nylon ®, Dynel ®, polypropylene, Dacron ®, and a cellulosic material in thickness from 0.8 to 12 mils were evaluated for use as a tape base. The physical characteristics of these nonwoven materials and other materials used are listed in Table 1. The initial selection of tape base materials was based on thickness, smoothness, flexibility, electrolyte wet-out and retention characteristics, and wet strength. Inertness to the oxidizing characteristics of the divalent silver oxide was also necessary. In addition to these requirements, the tape base porosity had to be such as to limit penetration of Ag_2O_2 during coating but allow electrolyte conductivity during discharge.

3. Cathode Active Material

The cathode active material, divalent silver oxide (<325 mesh) analyzed 96 wt-% divalent oxide as purchased from the Ames Chemical Works and was used without further treatment.

Since penetration of Ag_2O_2 through the base tape was undesirable, the particle size distribution of the Ag_2O_2 was important. This was determined by electron microscopy at our Dayton Laboratory.

Table 1

PHYSICAL DATA ON BATTERY MATERIALS

Product Designation	Name or Type of Material	Thickness mils	Weight g/in.²	Electrolyte Retention 30% KOH g/in.²	Manufacturer	Remarks
TAPES						
N561	Nonwoven nylon	3-4	0.034	0.135	Pellon Corp.	
2505K	Nonwoven nylon	5-6	0.038	0.115	Pellon Corp.	
2505	Nonwoven nylon	8-10	0.038	0.33	Pellon Corp.	
2505B	Nonwoven nylon	10-12	0.038	0.35	Pellon Corp.	
N524	Nonwoven nylon	60	0.032	0.80	Pellon Corp.	
EM403	Nonwoven Dynel	0.8	0.012	0.04	Kendall Co.	
EM436	Nonwoven Dynel	5-9	0.027		Kendall Co.	
EM476	Nonwoven Polypropylene	2.7	0.023	0.04	Kendall Co.	
EM485S	Nonwoven cellulosic	5	0.031		Kendall Co.	
MI410	Nonwoven Dynel	3.7	0.029	0.10	Kendall Co.	
OH 1.5	Porous Polyethylene	6-7	0.027	0.05	Millipore Filter	1.5 micron holes
OSIO	Porous Polyethylene	9-10	0.034	0.03	Millipore Filter	10 micron holes
GWA	Ion exchange membrane	5	0.038	0.19	Gelman Instrument	Nylon reinforced weak acid type, 5 micron holes (dry)
G PVA	Semipermeable membrane	5	0.038	0.04	Gelman Instrument	Nylon reinforced polyvinyl alcohol, 5 micron holes (dry)

BINDERS

					Manufacturer	Remarks
Gelvatol	R 20-30	Polyvinyl alcohol			Shawinigan Resins	Slow to wet with strong KOH
Methocel	R 65HG	Hydroxypropylmethyl cellulose			Dow Chemical	Very slow to wet with strong KOH
PVP K-30		Polyvinyl pyrrolidone			Antara Chemicals	Slow to wet with strong KOH
CMC 7HCP		Cellulose gum			Hercules Powder	Produced brittle coatings,
Acrysol		Polyacrylic acid			Rohm and Haas	slow to wet

ELECTROLYTES

KOH, 30% aqueous
KOH, 37% aqueous

CATHODE MATERIAL

Divalent silver oxide
  Ag2O2 content: 96 wt-%
  Silver content: 93 wt-%

CATHODE COLLECTOR

		Manufacturer	Remarks
Silver metal		Ames Chemical	325 mesh (44 micron)
Silver screen			

ANODE MATERIAL-ANODE COLLECTOR

		Manufacturer	Remarks
Silver metal		Handy and Harmon	Fine silver
Silver screen			
Zinc metal		New Jersey Zinc	Hi-grade
Zinc screen			
Zinc dust			

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The Ag_2O_2 powder was distributed in distilled water by ultrasonic agitation and a drop of the mixture was placed on a plastic-covered screen grid and allowed to dry. A series of 50 electron photomicrographs were taken of the particles. Each field was taken at random using three plastic-covered screen grids and magnifications from 1500X to 6000X.

The particles had three shapes: spherical, angular, and diamond. The particle size distribution was taken from 666 particles counted and measured. The longest dimension of the particle was used. The sizes ranges from 0.3 micron to 4.0 microns. The particle size distribution in 0.5-micron increments is given in Table 2.

Table 2

PARTICLE SIZE RANGE OF DIVALENT SILVER OXIDE

Range, microns	Per Cent	No. of Particles Counted
3.0	2.5	17
2.5-3.0	4.2	28
2.0-2.5	10.7	71
1.5-2.0	17.4	116
1.0-1.5	36.2	241
0.5-1.0	27.0	180
0.5	2.0	13

Thus, over 60% of the particles were in the 0.5- to 1.5-micron size range, considerably smaller than might be expected from screening through 325 mesh size (44 microns).

This range of particle size explains the penetration of Ag_2O_2 found in coatings on certain nonwoven fabrics and the reduction in penetration obtained by prewetting the fabric prior to coating as discussed in the following section.

4. Cathode Tape

Several methods of applying Ag_2O_2 to the tape base material were explored. Impregnation, pressing, and coating appeared to be feasible. Pressing of the Ag_2O_2 powder onto the base tape produced a tape with good discharge characteristics but handling and storage stability were lacking. Also, production of large quantities of continuous strips of tape would be inconvenient by this method. Impregnation of the base tape with an aqueous dispersion of Ag_2O_2 with binder was unsatisfactory for several reasons. The roughness and quantity of Ag_2O_2 in the resulting cathode tape depended on the base material used. Some base materials, such as porous polyethylene,

could not be impregnated at all. Also, impregnation would require the use of an additional separator tape. Dispersing Ag_2O_2 in a solution with a binder and coating with the resulting slurry appeared to offer the most flexibility in applying Ag_2O_2 to a wide variety of base materials in varying controlled thicknesses.

Initial attempts to coat a dry fabric were satisfactory with small strips, but prewetting of the fabric was found to be necessary in coating larger pieces of material. The fabric (5 x 30 in.) to be coated was saturated with distilled water on a glass plate. Excess water was then drawn off with a Gardner knife and the fabric was clamped lengthwise in slight tension. Using this technique the fabric remained dimensionally stable during coating and the tendency for Ag_2O_2 to penetrate the fabric was reduced. The Ag_2O_2 slurry was then drawn over the fabric with the Gardner knife to produce the desired coating thickness. The coating was air-dried in the dark at room temperature.

A typical coating solution had the following composition:

	Parts by Weight
Ag_2O_2*	30.9
Gelvatol ^{R} 20-30 (poly- vinylalcohol	5.6
Water (distilled)	63.7

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*Ag_2O_2, as used, analyzed 96% divalent silver oxide, which gives a coating composition of 85 wt-% Ag_2O_2 on a dry basis.

The coating solution was made by dispersing the Ag_2O_2 ultrasonically in water and adding the aqueous solution of binder with stirring. Satisfactory coatings were obtained with Ag_2O_2 content of 85 wt-% to as high as 92 wt-% (dry basis), depending on the nature of the surface being coated and the coating thickness desired.

Polyvinyl alcohol was selected as the binder (see Table 1) because it gave satisfactory operation and allowed fixing the design of the breadboard models at an early date. Other binders were tried with less satisfactory results.
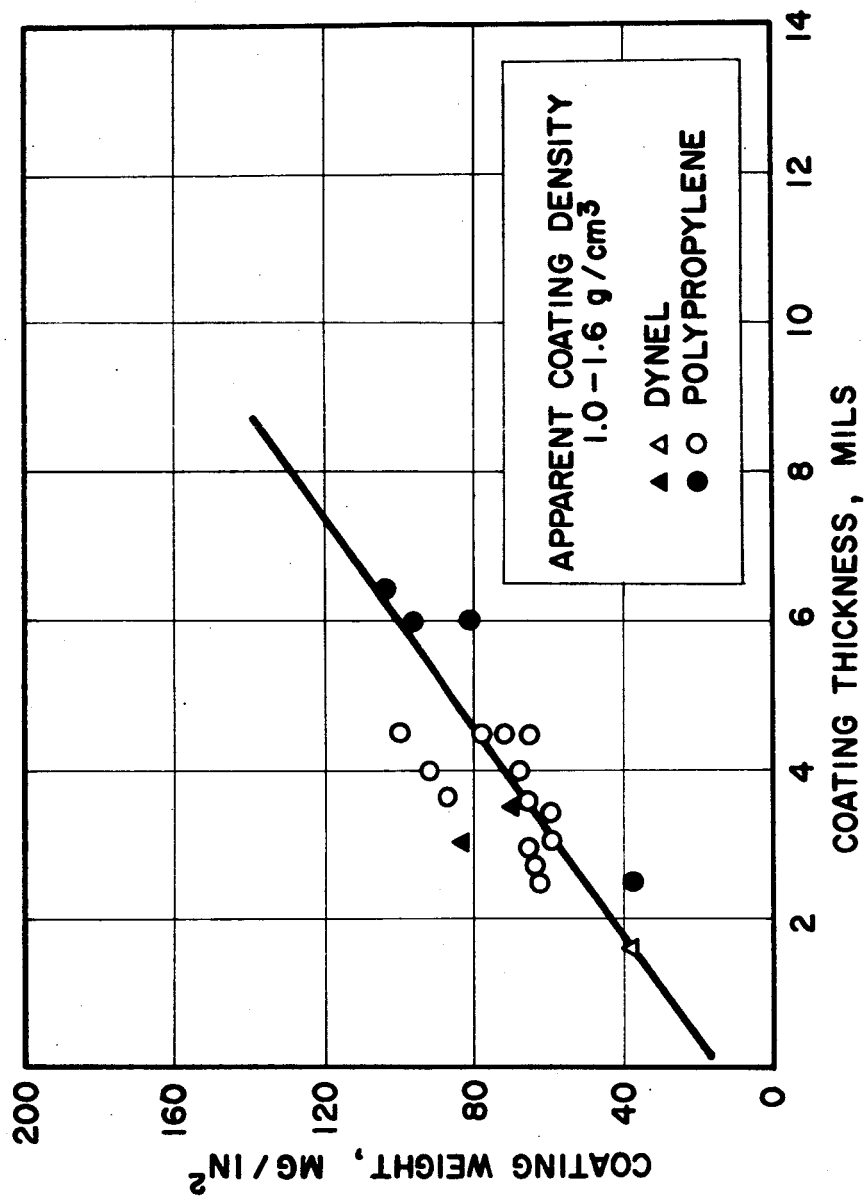
Figure 11. Coating Thickness and Weight for Satisfactory Ag₂O₂ Cathode Tapes

5. Cathode Coating Analysis and Tape Stability

The physical characteristics of the coated cathode tapes are given in Table 3. The makeup coating composition is given on a dry basis for comparison with the value obtained by analysis of the finished tape.

A considerable drop in Ag_2O_2 is apparent in many cases. This loss of Ag_2O_2 was reduced to a few percent in the later tapes by the use of forced air drying and protection of the coated tapes from light. All efficiency calculations were based on the as made up value rather than the measured percentage, making results conservative, rather than optimistic.

The range of coating thicknesses with satisfactory physical and discharge characteristics is shown in Figure 11 for Dynel and poly-propylene base materials. The thickest satisfactory coatings possessed an energy density of approximately 0.08 watt-hr/in.^{2} (260 watt-hr/lb coating). It is possible that a significant improvement could be made here since the apparent coating density was only in the order of 1.5 g/cm^3 (density of $Ag_2O_2 = 7$ g/cm^3). A more dense coating would provide higher capacity without an increase in coating thickness.

Coated tapes were tested for storage stability under ambient conditions and at 85°F and 88% relative humidity. Storage under ambient conditions with exposure to light of polypropylene base tapes with polyvinyl alcohol showed loss of Ag_2O_2 amounting to approximately 1 to 2% per month. Storage of the same type of tape at the high humidity and temperature gave losses of 30% in Ag_2O_2 in one month. The same coating on nylon-base tape showed a very large drop (un-analyzable) in Ag_2O_2 content and complete darkening of the underside of the tape in two weeks storage at the high temperature and humidity. Nylon is known to be less oxidation resistant then polypropylene. A similar tape with Methocel ® binder was more stable under the same conditions and showed only slight darkening on the underside of the tape. Thus, it appears that storage stability of the polypropylene base tapes should be satisfactory and perhaps the best storage stability would result from the use of Methocel binder.

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Table 3

PHYSICAL DATA ON COATED CATHODE TAPES

COATED ON PELLON (NON-WOVEN NYLON)

Tape	Base Material	Binder	Dry Thickness (mil)	Coating Composition (wt-%) Make-up	Ag₂O₂ Analysis	Total Dry Wt g/in.²	Ag₂O₂ Wt g/in.²	Comments
T-1	2505K	Gelvatol 20-30	16-25	-	-	-	-	Very rough surface
T-11	"	"	21-26	95	74	0.23	0.14	Impregnated, rough and dusty surface
T-20	N561	None	-	100	-	-	-	Pressed Ag₂O₂ into tape
T-2	"	Gelvatol 20-30	6-9	80	72	0.21	0.12	Fairly smooth
T-5	"	"	6-8	80	66	0.092	0.028	Fairly smooth
T-7	"	"	6-7	80	78	0.078	0.017	2 wt-% Conductex SC carbon black added, rough surface
T-8	"	"	9-11	80	-	-	-	2 wt-% Conductex SC carbon black added, rough surface
T-10	"	"	7-8	85	75	-	-	Fairly smooth
T-13	"	"	9-12	90	-	0.077	0.026	Fairly smooth
T-15	"	"	6-10	85	79	-	-	5 wt-% carbon black used (Aquablak 36)
T-17	"	"	8-10	90	-	0.17	0.11	Fairly smooth
T-18	"	"	8-10	Same as T-17				Fairly smooth
T-22	"	Methocel	5-7	94	88	0.10	0.054	Fairly smooth
T-27	"	Gelvatol 20-30	10-11	90	79	0.12	0.066	Fairly smooth
T-29	"	"	11-12	92	81	0.16	0.10	Fairly smooth
T-32	"	Methocel	11-14	92	76	0.18	0.11	Coating tends to crack
T-33	"	Gelvatol 20-30	10-12	92	69	0.21	0.12	Coating cracks
T-34	"	"	10-12	92	63	0.19	0.097	Smooth
T-35	"	"	8-10	92	59	0.17	0.080	Smooth
T-36	"	"	6-7	92	33	0.11	0.026	Rough, flakes off, inconsistent
T-26	2505	None (KOH)	-	-	-	-	-	Pressed dry KOH-Ag₂O₂ mix into tape
T-19	2505	Methocel	-	-	-	0.085	0.047	Pressed dry Methocel-Ag₂O₂ mix into tape
T-12	N524	Gelvatol 20-30	-	95	-	-	-	Impregnated, rough and dusty surface

Table 3 (continued)

Coated on Polypropylene (Non-Woven) EM476

Sample	Binder	Range					Appearance
T-24	M*	5-6	94	89	0.061	0.034	Smooth
T-28	M	10-12	90	80	0.104	0.066	Flakes off, smooth
T-31	G+M	8-10	85	51	0.104	0.041	Smooth
T-37	G	7-8	92	78	0.12	0.081	Smooth, flakes off
T-38	G	7-8	92	67	0.13	0.068	Granular
T-43	9G to 1M	9-10	90	84	0.13	0.085	Smooth
T-44 (M-16)	G	6-7	90	86	0.083	0.051	Somewhat granular
T-44 (M-17)	9G to 2M	8-10	90	85	0.12	0.086	Smooth
T-45	G	6-7	90	79	0.11	0.069	Somewhat granular
T-47	G	6-8	90	80	0.12	0.075	Smooth, cracks
T-49	G4 0-10	4-7	90	86	0.086	0.066	Granular, discolored
T-51	G	6-10	90	76	0.087	0.058	Smooth
T-52	G	7-8	90	84	0.10	0.068	Smooth, cracks
T-53	G	7-8	90	82	0.11	0.074	Smooth
T-54	G	5-8	90	79	0.095	0.056	Smooth
T-55	G	6-7	90	82	0.092	0.052	Smooth
T-56	G4 0-10	5-8	90	72	0.064	0.03	Smooth
T-57	G	5-7	90	83	0.083	0.052	Inconsistent
T-58	G	5-8	90	83	0.111	0.072	Very smooth
T-59	G	5-8	90	80	0.087	0.051	Smooth
T-60	G	5-7	90	82	0.089	0.051	Smooth
T-61	G	5-7	91.5	84	0.080	0.046	Smooth
T-62	G	4-5	91.5	84	0.077	0.045	Smooth
T-63	G	4-5	91	83	0.070	0.040	Smooth
T-64	G	5-7	91	84	0.074	0.041	Smooth
T-65	G	4-6	91	84	0.074	0.041	Smooth
T-66	G	4-6	91	82	0.070	0.040	Smooth
T-67	G	4-6	93	86	0.073	0.044	Smooth
T-68	G	5-7	93	83	0.079	0.044	Smooth

*M - Methocel, G - Gelvatol 20-30

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Table 3 (continued)

COATED ON OTHER BASE MATERIALS

T-3	OH 1.5	Gelvatol 20-30	11-12	-	22	0.11	0.018	Very smooth
T-4	GWA	Gelvatol 20-30	7-10	80	-	-	-	Smooth
T-6	EM403	S55L	3-4	80	50	0.051	0.018	Smooth
T-9	OS-10	S55L	-	-	-	-	-	Smooth
T-14	M1410	Gelvatol 20-30	11-15	85	87	0.10	0.062	5 wt-% carbon black used (Aquablak 36)
T-16	M1410	"	7-10	90	81	0.13	0.081	Fairly smooth
T-23	M1410	Methocel	5-6	94	89	0.074	0.042	Smooth
T-25	EM436	"	9-12	92	89	0.13	0.096	Rough, fibrous, tends to impregnate
T-30	EM403	"	7-8	92	53	0.084	0.032	Flakes off, smooth
T-40	EM485S	Gelvatol 20-30	10-12	92	32	0.12	0.03	Flakes off
T-41	FT2110	"	5-7	92	84	0.13	0.087	Greenish, smooth
T-42	M1365	"	10-12	92	62	0.14	0.059	Flakes off
T-50	EM403	" 40-10	3-5	90	82	0.095	0.067	Smooth, flakes off

C. METHOD OF ACTIVATION

To activate the dry tape, the aqueous electrolyte must be introduced just before the tape enters the current collectors. Micro-encapsulation offers an attractive solution to this problem but was not used in the feasibility demonstration owing to time limitations.

Instead, an uncoated tape prewet with electrolyte was used in addition to the coated tape. The prewet tape was stored in a container with a "pop-out" seal. Activation is accomplished by bringing the two tapes together just ahead of the current collectors. Operation in the dynamic tape test equipment indicates that the tapes using polyvinyl alcohol as a binder can be activated as close to the current collectors as desired.

Other methods of activation were also considered. A single dry tape was activated by drawing it over a wicking pad supplied with electrolyte by a metering pump. Incorporation of dry powdered KOH into the coated tape was also tried; water was supplied to activate the tape. Considerably longer activation times were necessary to allow dissolution of KOH and diffusion to form electrolyte. It was hoped that this could be done at the current collectors to take advantage of the heat effect to improve output, but the increased activation time seemed to obviate this possibility.

D. TAPE TEST PROCEDURE AND RESULTS

The main variables measured in the dynamic test device are summarized below:

Variable	Range of Typical Values
Current Density (discharge rate)	$0.15-1.7$ amp/in.^{2} (1- to 10-ohm load)
Electrolyte Feed Rate	$0.15-2$ cc/min
Tape Speed	$0.2-10$ in./min
Tape Pulling Force	$0.5-2$ pounds
Electrode Contact Pressure	$1-9$ ounces ($0.08-0.75$ lb/in.^{2})

The test equipment has been described in Section IIIA. A number of tape base materials and coating binders were subjected to pre-liminary screening using a simple static test requiring only a square inch of tape. The more promising combinations were tested further in dynamic operation. The results are given in Table 4. The preliminary dynamic test results are given in Appendix I.

Table 4

RESULTS OF LABORATORY TAPE TESTS

Conditions (Unless Specified): Electrolyte-37% KOH, Separator-2505B, "Dual Tape" Operation, 8 oz. Weight on Collector, Collector Area - Zinc 0.765 in.^{a}, Silver - 0.765 in.^{a}

Run No.	Voltage, Volts	Load Resistance ohms	Current Density^a amps/in.^{a}	amps/ft^a	Tape Speed, in./min	Time Maintained, min	Open Circuit Voltage	Remarks
T-5-44906	1.26	5	0.339	49	1	0.3	1.51	With Ag and Zn screens, 4 oz. wt.
T-6-27750	1.40	10	0.15	22	1	3		With and without Ag screen, 30% KOH
T-6-44901	1.30	3	0.45	65	1	2		
	1.30	10	0.138	20	1	0.25	1.52	
	1.10	2	0.55	79b	1	3		Ag and Zn screens, 4 oz. wt.
T-8-44902	1.40b	10	0.14b	20b	~0.3	1		Ag and Zn screens, 4 oz. wt.
T-9-44901	1.20b	10	0.10b	14b	1	2	1.52	Ag and Zn screens, 10 oz. wt.
	0.8b	10	0.08b	11b	1	2	1.56	Ag and Zn screens, 5 oz.wt. erratic
T-10-27750	1.34b	10	0.145	21b	0.5	2		Ag discharge
	1.0b	2	0.5	72b	1	2	1.56-1.58	Ag and Zn screens, Tape very slow to wet, single tape
T-11-44904	1.43	10	0.189	27	1	3		Same with Ag and Zn screen
T-12-44901	1.30	2	0.84	121	1		1.52	30% KOH, 2oz wt.
	1.45	10	0.145	21	1	0.2		30% KOH, 4oz wt.
	1.42	4	0.362	20	1	0.5		+ additional 30% KOH, 4oz wt.
	1.39	2	0.70	19	1-0.5	0.75		+ additional KOH, 4oz wt.
	1.30	1	1.29	21	1-0.5	0.75		+ additional KOH, 4oz wt.
			0.19					+ additional KOH, output drops off, 4 oz. wt.
T-13-44902	1.43b	2	0.86b	124b	1	4	1.55-1.59	Electrolyte Feed 0.3 cc/min., 2 oz. wt.
T-14-44906	1.26	10	0.17	24	1	3	1.52-1.56	Ag and Zn blocks appear clean after run, 2 oz. wt.
T-15-44906	1.40	10	0.17	24	1	0.5	1.52	voltage fluctuates, 30% KOH
T-16-44906	1.40	10	0.183	26	1	0.5	1.58	voltage fluctuates, 30% KOH
T-16-44904	1.08	10	0.185	27b	1	1	1.52	Ag screen
T-16-44904	1.36	2	0.65	94b	1	2		M1410 separator
T-16-44906	1.38	2	0.695	100	1	1		4 oz. wt., erratic discharge
T-19-44907	1.20	2	0.90	130	1	0.5	1.60	Ag screen
	1.34	1	0.912	131	0.5 - 3	0.1		Ag screen, pressed prior to discharge
	1.42	2	~1.56	~225	1	2		
T-20-44907	1.36	10	0.873	126	1	2	1.59	Ag screen, 2 oz. wt., 30% KOH
T-22-44907	1.22	4	0.189	27	0.5	0.5	1.63	Ag screen, 4 oz. wt., 30% KOH
	1.42	2	0.456	66	0.5	0.5	1.60	Ag screen, 4 oz. wt., 30% KOH
T-23-44908	1.42	10	0.808	116	1	0.5	1.61	Ag screen, slow to wet, 8 to 4 oz. wt.
	1.42b	6	0.195	28	1	0.5		Ag screen, slow to wet, 4 oz. wt.
	1.10b	1	0.323	46	1	0.5		
T-24-44908	1.47	10	1.40b	202b	1	1	1.6-1.63	no screen-additional pressure required
	1.30b	2	0.20b	27b	0.5-1	3		
T-25-44908	1.38	10	0.86b	124b	1	-	1.62	Tape somewhat rough, slow to wet, 4 oz. wt.
	1.12	2	0.192	28	1	2.5		
T-26-44908	0.70a	10	0.73	105	1	-	1.10	4 oz. wt., distilled water wet separator
			0.098	14				

a Based on area of smaller collector
b Average value

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Table 4 (cont).

RESULTS OF LABORATORY TAPE TESTS

Conditions (Unless Specified): Electrolyte-37% KOH, Separator-250B, "Dual Tape" Operation, 8 oz. Weight on Collector, Collector Area - Zinc 0.765 in.^{2}, Silver - 0.765 in.^{2}

Run No.	Voltage, Volts	Load Resistance ohms	Current Density[a] amps/in.^{2}	Current Density[a] amps/ft^2	Tape Speed in./min	Time Maintained min	Open Circuit Voltage	Remarks
T-26-44908 (continued)	1.47	10	0.204	29	1-0.5	0.4	1.61	Added electrolyte at current collector
	1.40	4	0.475	68	0.5	0.5		Added electrolyte at current collector
	1.38[b]	2	0.92	132	1	1		Added electrolyte at current collector
	1.28[b]	2	1.70[b]	245[b]	1	0.5		Added electrolyte at current collector
T-27-44909	1.34	2	0.88	127[b]	1	1.5	1.59	Electrolyte feed, 0.35 cc/min.
	1.26[b]	1	1.68	230[b]	1	2		
T-27-44912	1.42	10	0.18	26	1	0.5	1.56	4 oz. wt. saturated LiOH electrolyte, coating tends to soften and scrape off.
	1.35	4	0.45	65	1	0.5		
	1.26	2	0.82	118	1	5.0		
T-29-44912	1.26	2	0.82	118	0.75	3.5	(4oz.wt.) 1.63	37% KOH added
T-33-44912	1.32[b]	2	0.88[b]	126	1	4	(4oz.wt.) 1.58	Rises to 0.90 amp/in.^{2} and 1.38 volts on stopping tape momentarily. Stopped tape 30 min with load connected. Zinc surface darkened. Resumed tape speed of 0.5 in./min and output returned after 10 min. to 0.84 amp/in.^{2} and 1.26 volts.
	1.32[b]	2	0.86[b]	124	1	15		
T-33A-44912	1.34[b]	2	0.88[b]	126	0.5	15	1.58	Stopped tape 45 min on open circuit. Zinc remained clean, output resumed. 0.33 cc electrolyte/in.
T-32-44913	1.42	8	0.25	36	0.5	2	1.60	Drops off after 1 min, zinc fouled at rear of collector. 0.33 cc electrolyte/in.
	1.40	4	0.36	52	0.5	3		
	1.39	3	0.61	88	0.5	2		
	1.30	2	0.85	122	0.5	1		
T-57-44913	1.47	10	0.20	19	0.25	2.5	1.64	0.3 cc electrolyte/in.
	1.465	8	0.25	36	0.25	2		
	1.455	6	0.33	47	0.25	3		
	1.43	4	0.48	69	0.25	6		
	1.40	3	0.621	89	0.25	5		
	1.32	2	0.85	122	0.25	1		Drops off during 1 min.
	1.32	2	0.86	124	0.5	1		Drops off after 1 min.
	1.34	2	0.88	126	1	2		

a Based on area of smaller collector

b Average value

Table 4 (cont).

RESULTS OF LABORATORY TAPE TESTS

Conditions (Unless Specified): Electrolyte-37% KOH, Separator-250SB, "Dual Tape" Operation, 8 oz. Weight on Collector, Collector Area - Zinc 0.765 in.², Silver - 0.765 in.²

Run No.	Voltage, Volts	Load Resistance ohms	Current Density[a] amps/in.²	Current Density[a] amps/ft²	Tape Speed in./min	Time Maintained min	Open Circuit Voltage	Remarks
T-37-44914	1.30	2	0.85	122	1.0	3	1.60	
	1.30	2	0.85b	122	0.25	2		
	1.32b	2	0.86b	124	1.0	5		Output drops off after 2 min.
T-44M16-44914	1.45	8	0.25	36	0.27	8	1.64	
	1.43	6	0.32	46	0.27	8		
	1.38b	4	0.46	66	1.0	2.5		
T-44-M17-44914	1.45	2	0.88b	126	1.0	5		
	1.40	8	0.25	36	0.27	0.5	1.64	
	1.37	4	0.47	68	0.27	1		
	1.44	2	0.87	125	1.0	2		Slight discoloration at one corner of zinc.
T-44M16-44914	1.46	6	0.32	46	0.2	12	1.65	
T-17-44915	1.32b	8	0.86	124	0.2	9	1.62	
	1.46	2	0.25	36	1.0	7		
	1.45	8	0.48	69	0.5	5		
	1.42	4	0.91	131	0.5	2		
T-44M16-44915	1.48-1.42	2	0.38-0.37	54	0.7	15	1.63	Output drops off after 2 min. Zinc partly coated with blue deposit.
	1.46b	8	0.25b	36	0.5	20		
	1.36b	2	0.89b	128	0.65	4		
	1.25b	1	1.56	216	1.4	0.5	1.64	
T-45-44915	1.45	8	0.25	36	1.0	Steady	1.62	
	1.39b	2	0.90b	130	1.0	3		
	1.36	1	0.90b	130	0.9	20		
	1.28b	4	1.76	245	<2	1		
T-47-44916	1.2b	4	0.38b	55	1	10	1.58	Large fluctuations.
	1.1b	2	0.72	104	1	5	1.64	Large fluctuations. Stopped tape 1 hr. with Ag electrode removed.
	1.43	4	0.48	69	0.5	2	1.63	Output drops off.
	1.34	2	0.88	126	0.5-0.75	2		
	1.40	4	0.47	67	0.35	7		
T-47A-44916	1.43	8	0.25	36	0.25	5	1.60	Very erratic output after 5 min.
T-48-44916	1.42b	8	0.25b	36	0.5	2	1.62	30% KOH, 4 oz. on collector.
T-49-44916	1.30b	4	0.45b	65	1	20		Very erratic output, with and without Ag screen.
	1.46	8	0.25b	36	0.25	2	1.62	E 1.46 1.43 1.35
	1.4b	-	0.55b	79	0.5	10		C.D. 0.33 0.48 0.88 0.5 lpm.

a. Based on area of smaller collector

b. Average value

Table 4 (cont).

RESULTS OF LABORATORY TAPE TESTS

Conditions (Unless Specified): Electrolyte-37% KOH, Separator-2505B, "Dual Tape" Operation, 8 oz. Weight on Collector, Collector Area - Zinc 0.765 in.², Silver - 0.765 in.²

Run No.	Voltage, Volts	Load Resistance ohms	Current Density [a] amps/in.²	amps/ft²	Tape Speed in./min	Time Maintained min	Open Circuit Voltage	Remarks
T-50-44916	1.4	2	0.91	131	1	5	1.64 (4ozwt.)	Electrodes not cleaned prior to run (after T-49)
	1.44	8	0.24	34	0.2	1		
T-49A-44916	1.48	8	0.25	36	0.2	1	1.65	E 1.47 1.46 1.45 0.51pm / C.D. 0.25 0.33 0.48 / E 1.46 1.43 / C.D. 0.33 0.48
T-51-44917	1.44	3	0.64	92	0.75	10		Output drops off after 8 min. Output drops immediately on 2 lead, zinc fouled.
	1.40	2	0.91	131	1	3		
	1.3b	-	1.04b	150	1	3		
	1.44b	8	0.25b	36	0.2	10		
	1.43b	6	0.33b	47	0.2	8		
	1.39b	4	0.43b	62	0.3	8		
T-52-44917	1.40	-	0.62	89	0.4	7	1.62	Output erratic
	1.26b	-	.95b	137	0.75	3		Test on tape deck.
	1.18	-	1.21	175	1.0	5		
T-53-44917	1.43	8	0.58	83	0.25	1	1.62	Output after 5 min. 0.328 in.² zinc.
	1.40	-	0.90	130	1	1		
	1.32	-	1.5	216	0.75	15		
T-55-44918	1.4	4	0.37	53	0.2	15	1.60	0.985 in.² zinc, 30% OH
T-54-44918	1.46	8	0.20	29	Output erratic		1.62	0.985 in.² zinc
T-44-44918	1.44	8	0.20	29				0.985 in.² zinc
	1.40b	4	0.37b	53				0.985 in.² zinc
T-57-55918	1.45	8	0.20	29	0.25		1.62	0.985 in.² zinc
	1.44	6	0.26	37	0.2	30		0.985 in.² zinc
T-60-44918	E 1.44 1.42 1.39				0.2		1.64	0.328 in.² zinc
	C.D. 0.58 0.76 0.91							
T-60-44918	E 1.47 1.44						1.65	0.985 in.² zinc
	C.D. 0.20 0.38							
T-63-44919	1.46-1.4	8	0.26-0.25	36	0.23	8	1.65	Output dropping off.
	1.44	6	0.33	47	0.23			
	1.45	4	0.34	49	0.4			
	1.40	4	0.48	69	0.9			
	1.43	4	0.49	70	0.9			
T-62-44919	1.46-1.4	8	0.26-0.25	37	0.23		1.66	25 oz. wt. on collector.
	1.40	4	0.48	69	1			Pressed section of tape
	1.20	2	0.81	116	1			
	1.18	2	0.80	115	0.87			
	1.14	2	0.79	114	0.75			

a Based on area of smaller collector

b Average value

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The tests were carried out primarily to determine the general characteristics of a tape system and to obtain an operable tape for use in the feasibility demonstration. Since recurrent modifications on the test equipment and coating methods were made, direct comparison of all test results is not possible. For example, the current collectors were decreased in width to 7/8 in. and redesigned to reduce alignment problems in the "dual-tape" system.

The test procedure consisted of initial determination of the open circuit voltage followed by discharge at increasing rates to determine the maximum discharge rate obtainable at a fixed tape speed. A tape speed of 1 inch per minute was the maximum used in most of the tests. If a steady discharge was maintained for the time required to pass twice the collector length, the discharge rate was increased further (usually doubled) by decreasing the load resistance. While this discharge time probably did not bring the tape to steady-state conditions, it did provide for a complete change of depolarizer at the collectors.

Later tests were run on full lengths (approximately 25 in.) of tape at a fixed discharge rate and with intermittent operation.

While complete detailed experiments have not been conducted to provide mathematical relations for the variables involved, a number of general correlations and observations have been made. Assuming a fixed tape speed with excess electrolyte supplied, the maximum discharge rate maintainable depends primarily on the percentage of Ag_2O_2 in the coating and the type of material used for the separator and coating cupport. Loss of output voltage was most often due to penetration and deposition of silver on the zinc collector. As the percentage of Ag_2O_2 in the coating decreased with the same type of tape, lower output voltages were obtained.

Coating uniformity and smoothness must be such that the collector contacts essentially all the coated area beneath it. With a screen or roller collector, more roughness could be tolerated. Increasing pressure on the current collectors increased output only momentarily when good contact was already being made. A force of 2 to 5 ounces was generally sufficient for good contact with smooth tape. Most often, a weight of 8 ounces was used to give good contact with a wide range of tapes. When there was excess Ag_2O_2 on the tape for the conditions used, slowing or stopping the tape usually produced a small rise in output, at least temporarily. This is believed due to better contact with and improved conductivity of the discharging coating.

The use of very thin (1-3 mil) permeable nonwoven materials allowed high discharge rates to be attained, but failure due to zinc fouling was rapid in many cases. Materials of low permeability eliminated the fouling but also limited discharge severely. The best compromise was the use of a thick (10 mil), highly permeable separator/electrolyte feed tape with a thin (1-3 mil) coated tape. The use of hydroxymethylcellulose as a binder seemed to limit migration of silver and degradation of Ag_2O_2 during coating. However, the resulting coating was slow to wet with electrolyte, requiring a longer contact length with electrolyte tape or a slower tape speed.

The test results for the most similar tapes are compared in Table 5. The last two lines of the table give the energy density in watt-hr/lb for the dry Ag_2O_2 coated tape above, and for the tape system including the separator and 1.1 times the theoretical amounts of 37% KOH and zinc. The energy densities calculated with 1.1 times the theoretical amount of zinc and the electrolyte actually supplied range from 20 to 40 watt-hr/lb. As can be seen the cathode utilization is high, even at current densities near 1 amp/in.^{2} although a drop off at high current density is apparent.

The relationship between the maximum output voltage and current density obtained from various tapes is shown in Figure 12. The anode area varied from 0.328 in.^{2} to 0.985 in.^{2}. In all cases, even though the anode area was changed, the voltage-current density relationship remained constant.

It should be noted that the open circuit voltage was approximately 1.6 to 1.65 volts, considerably below the 1.86 open circuit potential of primary silver-zinc batteries. This has recently been shown to be caused, at least in part, by the silver current collector, where reaction of divalent silver oxide with metallic silver can take place to form the lower potential monovalent oxide. Substitution of an inert (gold-plated) collector resulted in an open circuit voltage of the expected value. At a current density of 1 amp/in.^{2}, the output voltage was about 1.4 volts, giving a voltage drop due to internal resistance of about 0.1 volt.

The utilization of silver peroxide as a function of current density is shown in Figure 13, which represents the best results obtained. At a current density of 1 amp/in.^{2}, a cathode utilization of 85% was obtained; this was calculated on the "as-coated" weight of silver peroxide. Again, the most critical requirements for obtaining high cathode utilization appear to be (1) a smooth coating with a minimum of binder present and (2) matching tape speed to drain rate.

Table 5

SUMMARY OF RESULTS OBTAINED IN TAPE TESTS WITH LABORATORY TESTER

| Base Material	Polyproplene								Nylon			Dynel
Tape No.	T-63	T-57	T-37	T-60	T-24	T-44A	T-52	T-44	T-22	T-13	T-27	T-6
Current Density amp/ft^2	36	37	89	110	124	127	175	216	116	122	230	91
Tape Speed in./min	0.25	0.2	0.25	0.2	0.75	0.6	1.0	1.4	0.5	1.0	1.0	1.0
Cathode Utilization %	88	98	94	92	98	90	62	70	98	78	75	83
Energy Density Watt-hr/lb of Ag$_2$O$_2$ coated tape	156	190	188	174	170	156	103	111	137	94	108	54
Watt-hr/lb of Reactants including separator, and 110% theo. zinc and electrolyte	63	58	54	67	58	64	44	48	55	55	49	29
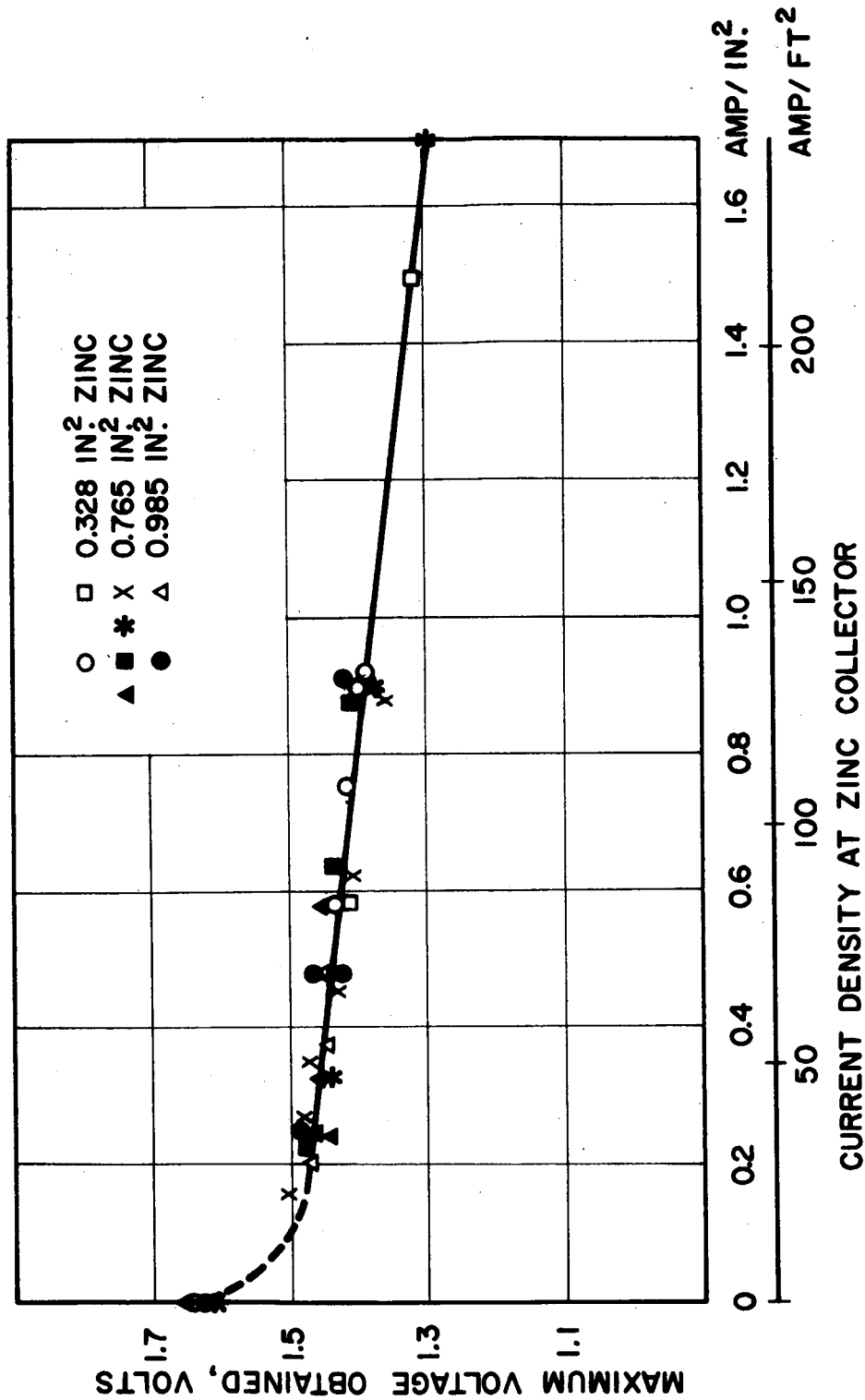
Figure 12. Maximum Voltage as a Function of Current Density at the Zinc Anode
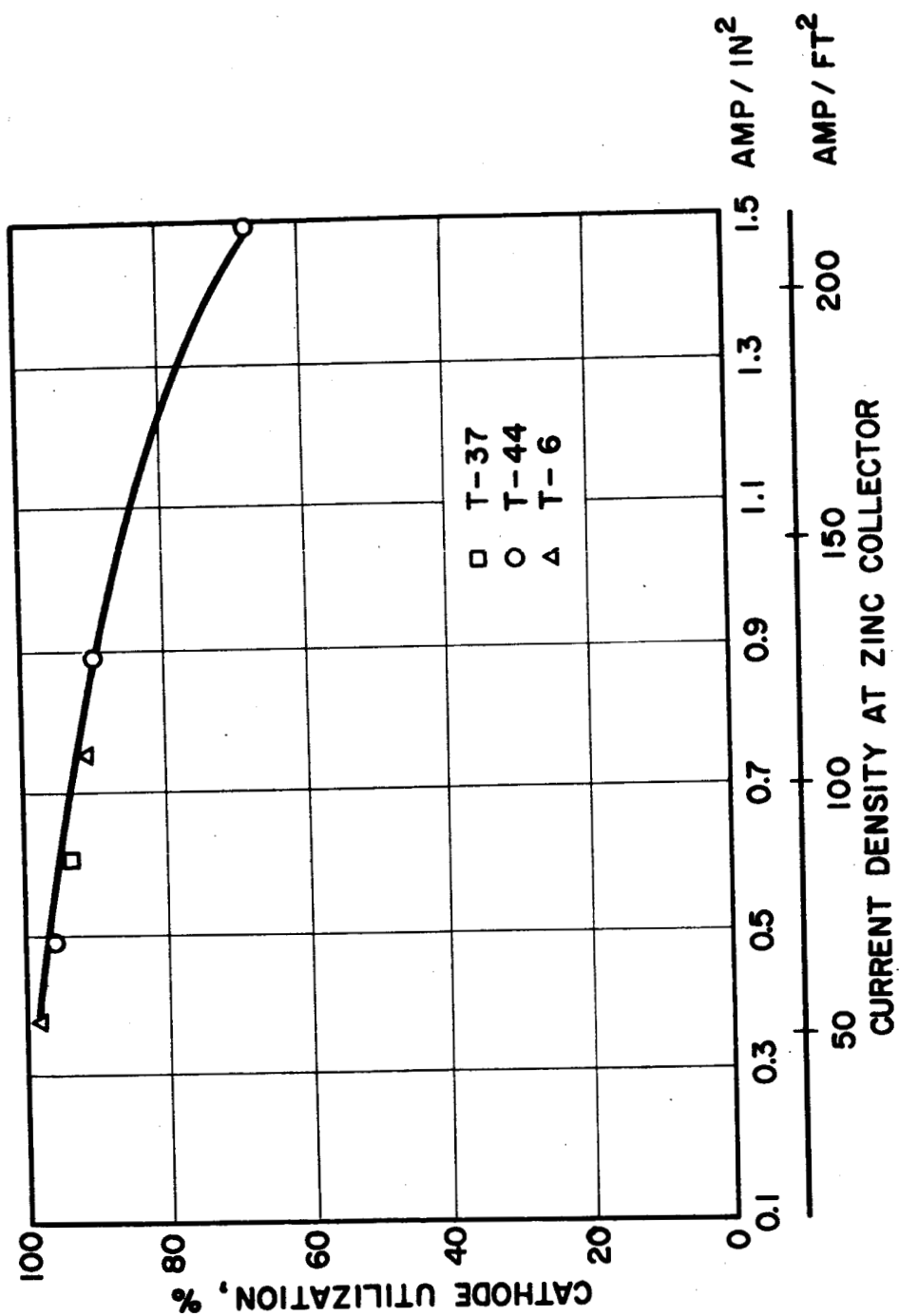
Figure 13. Utilization of Silver Peroxide as a Function of Current Density

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The current densities as functions of the tape speed for various
tape bases and coating thicknesses are shown in Figures 14 to 16.
For any coating thickness and tape speed there is a theoretical
maximum current that can be drawn from the system. This is shown by
the straight line portion of the plots and is labeled 100% cathode
utilization. The actual test results are shown by the curved lines.
The deviation of the curved line from the 100% utilization line gives
an indication of the current efficiency at any tape speed. The
current densities plotted on the vertical scales are the maximum ones
obtained with a steady voltage output.

Two interesting points are noted in Figure 16. First, in the 3- to 4-
mil coatings, the actual current densities do not fall off as
drastically from the 100% utilization line as they did with the 3-
to 4- mil coatings in Figure 15. This is probably due to a non-
uniformity in the coating technique.

Secondly, the curves for the 5- to 6- mil coatings show a drastic
leveling off when compared with the 100% utilization line. Several
explanations are possible. This may again be due to a nonuniformity
in the coating technique or it could mean that a limiting thickness
of coating was reached beyond which more active materials could not
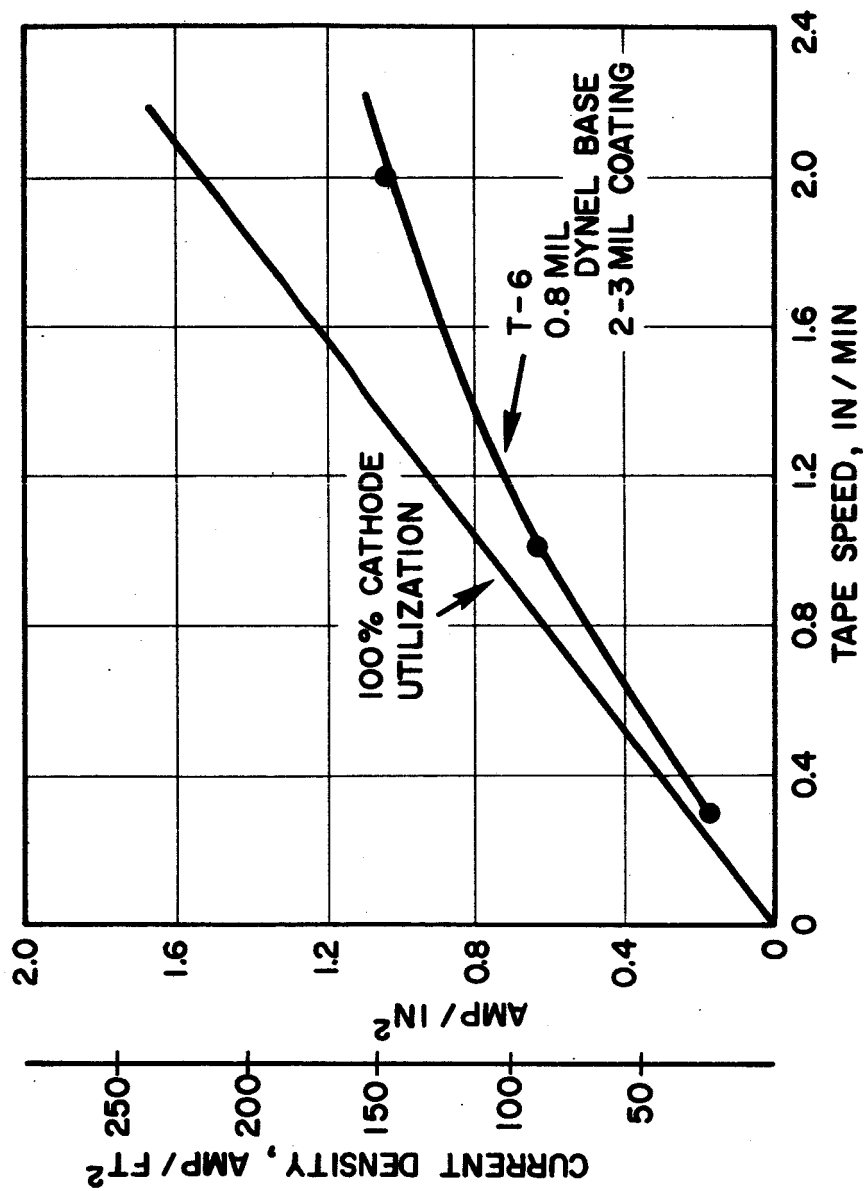be efficiently utilized at high speeds.

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Figure 14. Effect of Tape Speed and Current Density on Cathode
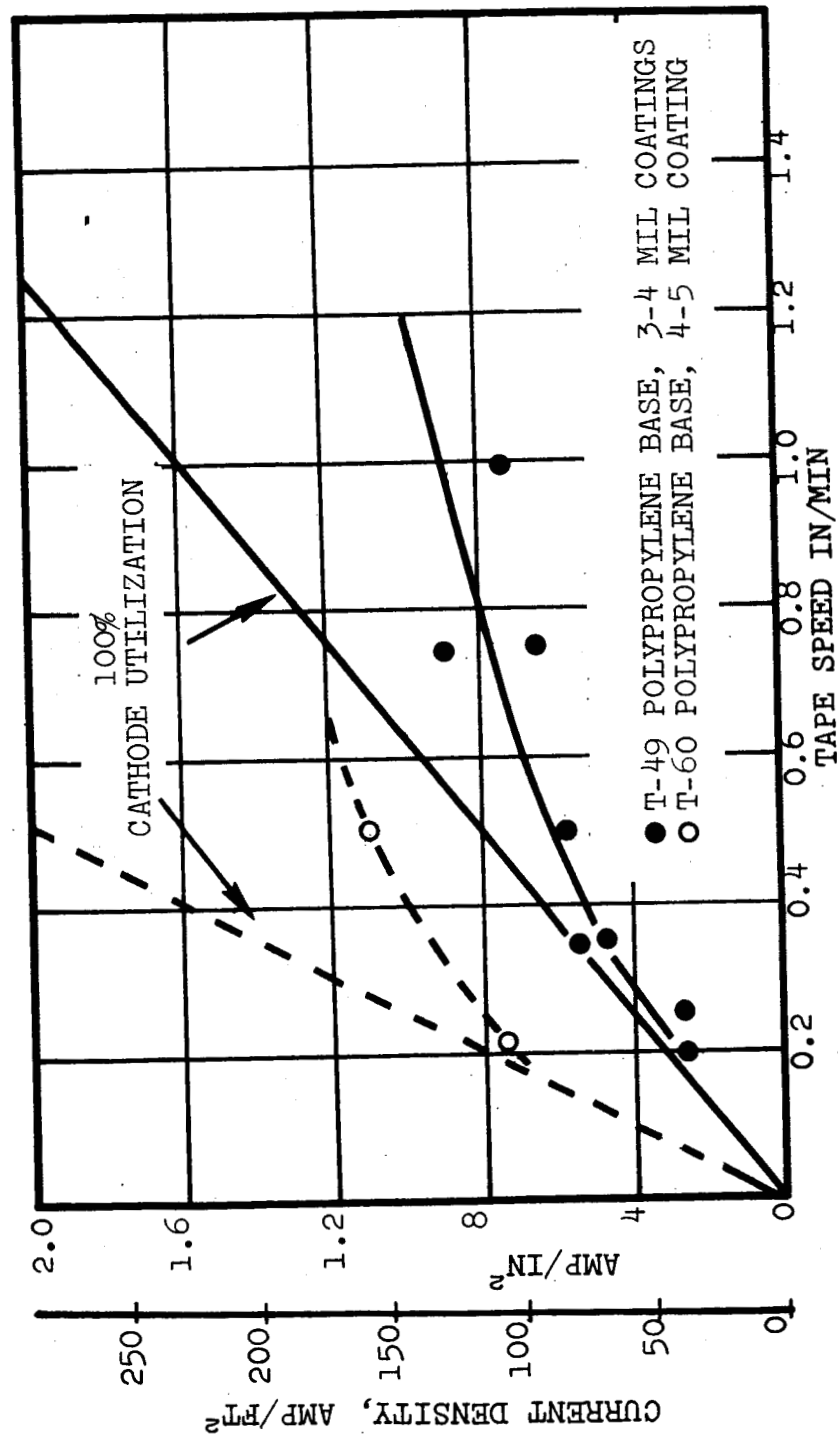Utilization, Tape T-6

43

Figure 15. Effect of Tape Speed and Current Density on Cathode
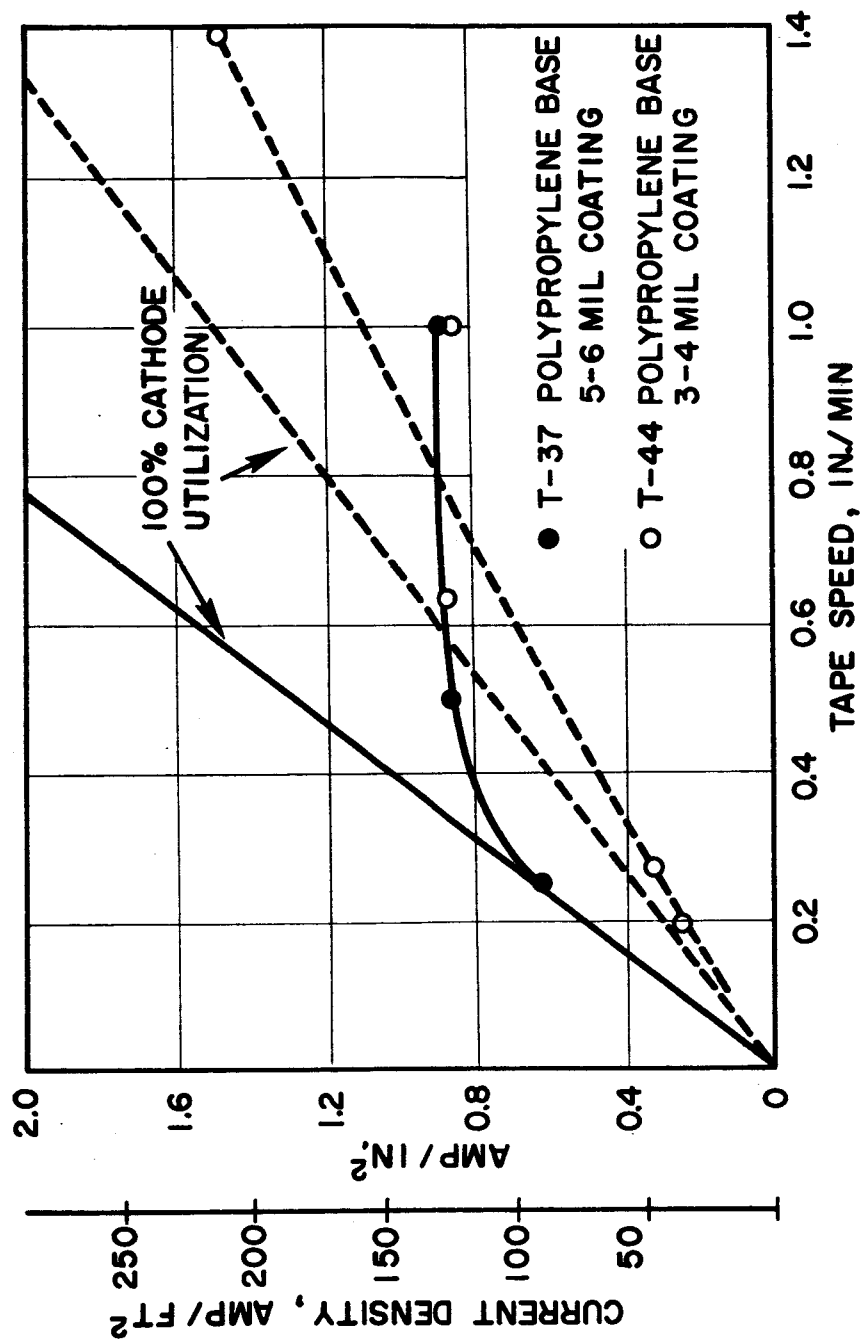Utilization, Tapes T-49 and T-60.

44

Figure 16. Effect of Tape Speed and Current Density on Cathode Utilization, Tapes T-37 and T-44

V. PHASE II-PROOF, DEMONSTRATION, AND DELIVERY

The feasibility of the dry tape battery concept was demonstrated on the laboratory test device and with the breadboard demonstration units which were delivered. In fulfillment of the contract, 4 breadboard demonstration units and 16 spare tape decks, each loaded with approximately 25 minutes of tape, were delivered. Figure 17 is a photograph of one of the final devices.

A. DRIVE TESTS

Prior to delivery, each of the 4 breadboard demonstration unit drives were tested with and without tapes. To prove satisfactory performance with tapes, a total of 20 tape decks were tested in the 4 drives.

Each drive unit was given the following tests:

1. Without the escapement mechanism assembled, the spring motor was wound 22 times and allowed to run down completely. The purpose of this check was to determine whether each spring motor had the required energy storage capacity.

2. Also without the escapement mechanism, the spring motor was wound 1/2 to 1 turn of the key. The motor was required to operate with this minimum number of turns to show that the frictional forces were minimal.

3. One complete drive was wound the full 22 turns of the key and its rundown period was timed at 144 minutes, which was well in excess of the 25-minute tape deck operation required.

4. With the escapement mechanism assembled, the spring motors were tested with 4 turns of the key. The complete motor was required to operate with this minimum number of turns to show that frictional forces were minimal.

B. TAPE TESTS

All 20 tape decks were tested with approximately 25 inches (25 minutes at 1 inch per minute) of active tape. During the operation of each tape deck the current-voltage characteristics were measured and recorded. Figure 18 shows the range of values obtained during these tests.

Following this test, each tape deck was reloaded and the current collectors were cleaned. The electrolyte tape containers were then sealed and the tape decks packaged and shipped.
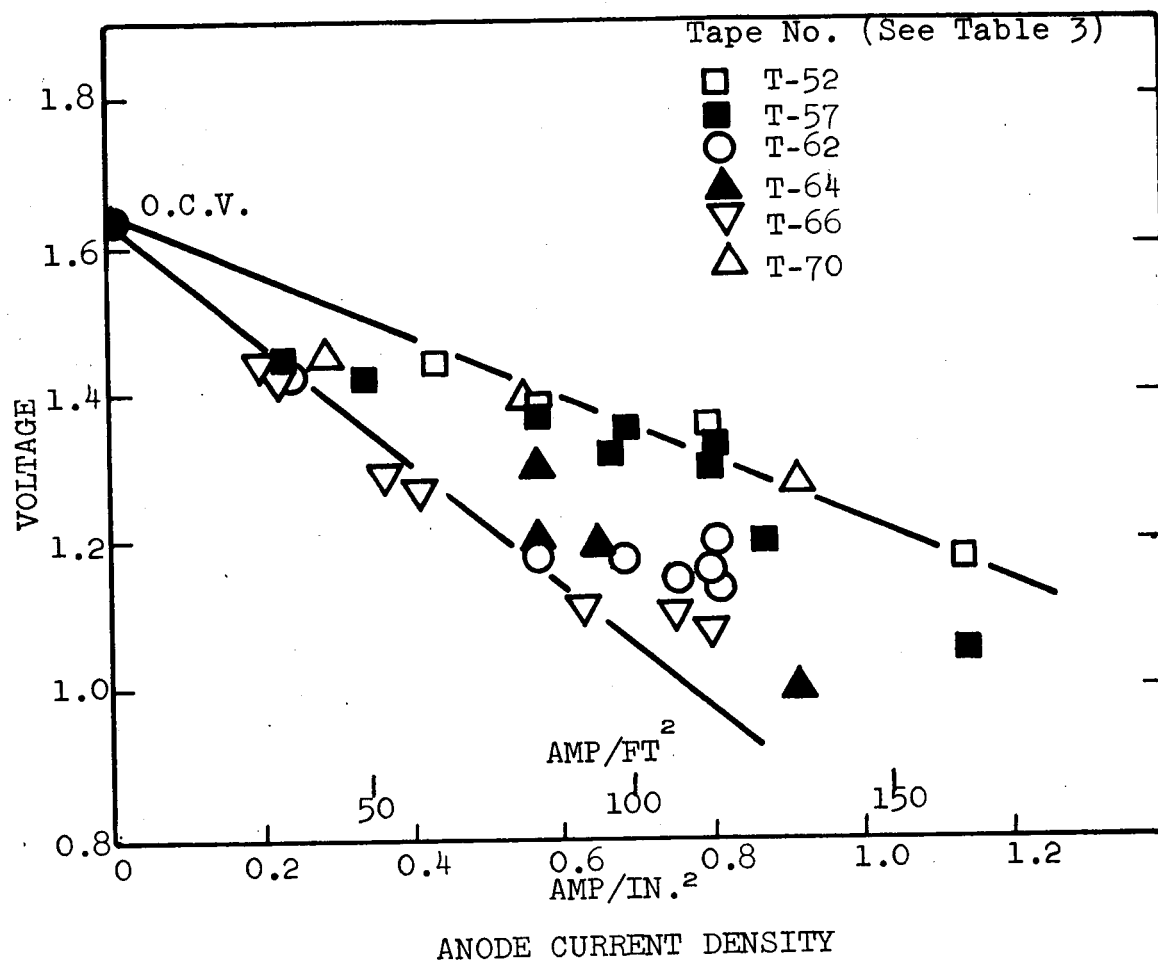
46

Figure 17. Final Demonstration Model Dry Tape Battery

Figure 18. Operating Range of Tapes Tested in Completed Tape Decks.

PRELIMINARY TAPE TEST RESULTS ON LABORATORY TESTER

Run No.	Separator	Voltage Volts	Load Resistance ohms	Current Density[a] amps/in.²	amps/ft²	Tape Speed in./min	Time Maintained min	Open Circuit Voltage	Remarks
T-1-27746	None	1.51	10	0.075	11	1	1	1.56	Poor contact due to rough tape surface, 2 in.² zinc
	None	1.39	2	0.355	51	1	2		
T-1-27748	2505	1.50	10	0.16b	23b	1	0.5		Gold roller cathode collector
	2505	1.40	3	0.49b	70b	1	1		Gold roller cathode collector
	2505	1.40	2	0.72b	104b	1	0.5		Gold roller cathode collector
T-2-27746	None	1.20c	10	0.20c	29c	1	2	1.56	1 in. zinc
	2505	1.14	1	1.1	158	10	0.1	1.65	Additional Ag₂O₂ spread
	2505	1.32	4	0.28	40	2	-		Additional Ag₂O₂ spread
	2505	1.24	2	0.57	82	2			Additional Ag₂O₂ spread
T-2-27747	None	1.50	5	0.25	36	1		1.50	Ag screen cathode collector
	None	1.40	2	0.65	93	1			Ag screen cathode collector
	None	1.30	1	1.23	177	1	0.5	1.55	Ag screen cathode collector
	2505K	1.46	10	0.14	20	0.2	3		Ag screen cathode collector
	2505K	1.20	2	0.56	81	0.5	2	1.58	Ag screen cathode collector
	2505K	1.49	2	0.65b	93b	1			Ag screen cathode collector and Zn strip anode
	2505K	1.24	2	0.62	89	1	2	1.58	Ag screen cathode collector
T-3-27746	None	1.29	1	0.63	91	1	2		Ag screen cathode collector
T-4-27748	2505B	1.49	10	0.16	23	1	0.5	1.66	"Dual Tape" system
T-4-27749	None	1.50	10	0.16	23	1	0.5	1.52	Zn screen anode
T-5-27749	None	1.36	10	0.13	19	1	-	1.54	With and without Ag screen cathode
	N561	1.30	6	0.23	33	1	-	1.54	With and without Ag screen cathode and Zn screen

a Based on area of smaller collector

b Actual current

c Average value

APPENDIX II

REPORT ON WORK DONE FROM

19 DECEMBER 1963 TO 23 JANUARY 1964

APPENDIX II

REPORT ON WORK DONE FROM
19 DECEMBER 1963 TO 23 JANUARY 1964

A. INTRODUCTION

Our future plans in this work will comprise continued development
of the system into a more applicable end device as well as further
research into exotic high energy couples for incorporation into the
electrode structure. Among the specific tasks to be accomplished
are to:

1. Devise methods of incorporating high energy anodes and cathodes
    into tape systems,

2. Investigate various methods of encapsulating electrolyte,

3. Combine the highest possible energy couple into the one tape
    configuration.

4. Design a tape conversion device capable of supplying its own
    power for unattended operation, and

5. Work out methods of supplying multiple cell voltages for the
    dry tape battery.

Progress on these tasks during the period 19 December 1963 to 23
January 1964 is discussed in this report.

B. HIGH ENERGY ANODES AND CATHODES

1. Analysis of Projected Capabilities

One particular example of high energy density system is the magnesium/
meta-dinitrobenzene couple. This seems to be ideally suited to our
purposes since, in a primary battery configuration, its output is
limited by mass transport or diffusion rather than by thermodynamics.
In present primary battery usage, it is a high energy density couple,
capable only of low drain rates. Applying this couple to a tape
could considerably improve its drain capabilities since the diffusional
limitation is overcome by mechanically feeding the reactants to the
reaction sites.

The magnesium/meta-dinitrobenzene couple has a theoretical energy density
of 766 watt hours per pound of reactants, a figure which includes the
8 moles of water required in the reduction of each mole of meta-dini-
trobenzene.

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Figures 19(a) and (b) show the results of a system analysis based on the magnesium/meta-dinitrobenzene couple applied to the tape. The graphs show the total system weight in ounces as a function of mission time for individual periods of operation of 10, 100, 1,000, and 10,000 hours and for 5 years. For each case the tape feed rate is one inch per minute and the current output is 5 amperes for the entire mission time. In each case the mechanical components for the entire system are scaled up versions of those used for the 10-hour mission.

Considering the 10-, 100-, and 100-hour mission times [Fig. 19(a)], it is seen that:

1. The electrolyte capsule weight goes from 22 to 14 to 7.5 per cent of the total weight.

2. The weight of the case goes from 19 to 13 to 13 per cent of the total weight.

3. The weight of the drive goes from 36 to 15 to 2.5 per cent of the total weight.

4. The reels are constant at 3% for the 10-hour and 100-hour levels but rise to 6 per cent of the total weight for the 1000-hour mission.

5. The weight of the electrolyte rises from 6 to 17 to 22 per cent of the total weight. Here it should be noted that the dotted line represents the dividing point between the water required for the reaction of meta-dinitrobenzene and that of the electrolyte. It can be seen that the weight of the water of reaction is larger that that assumed for electrolyte. This proportionality is also carried but not too clearly seen in the 10- and 100-hour mission times.

6. The weight of the coated tape as a fraction of the total system weight rose from 14 to 38 to 49 per cent.

For the 10-hour mission the total energy density is calculated to be 67 watt-hours per pound; for the 100-hour mission it is 185 watt-hours per pound; for the 1000-hour mission it is 235 watt-hours per pound.
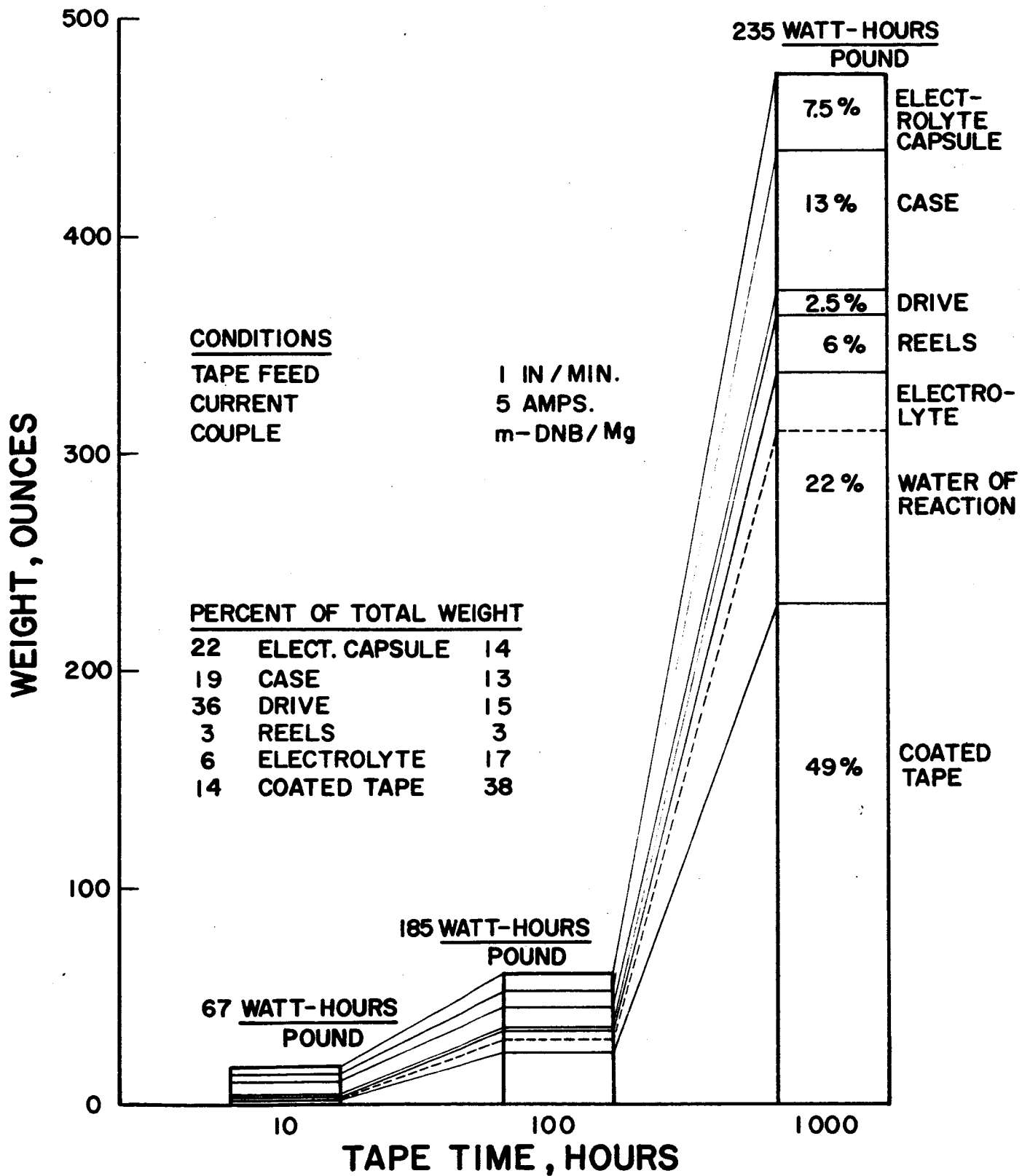
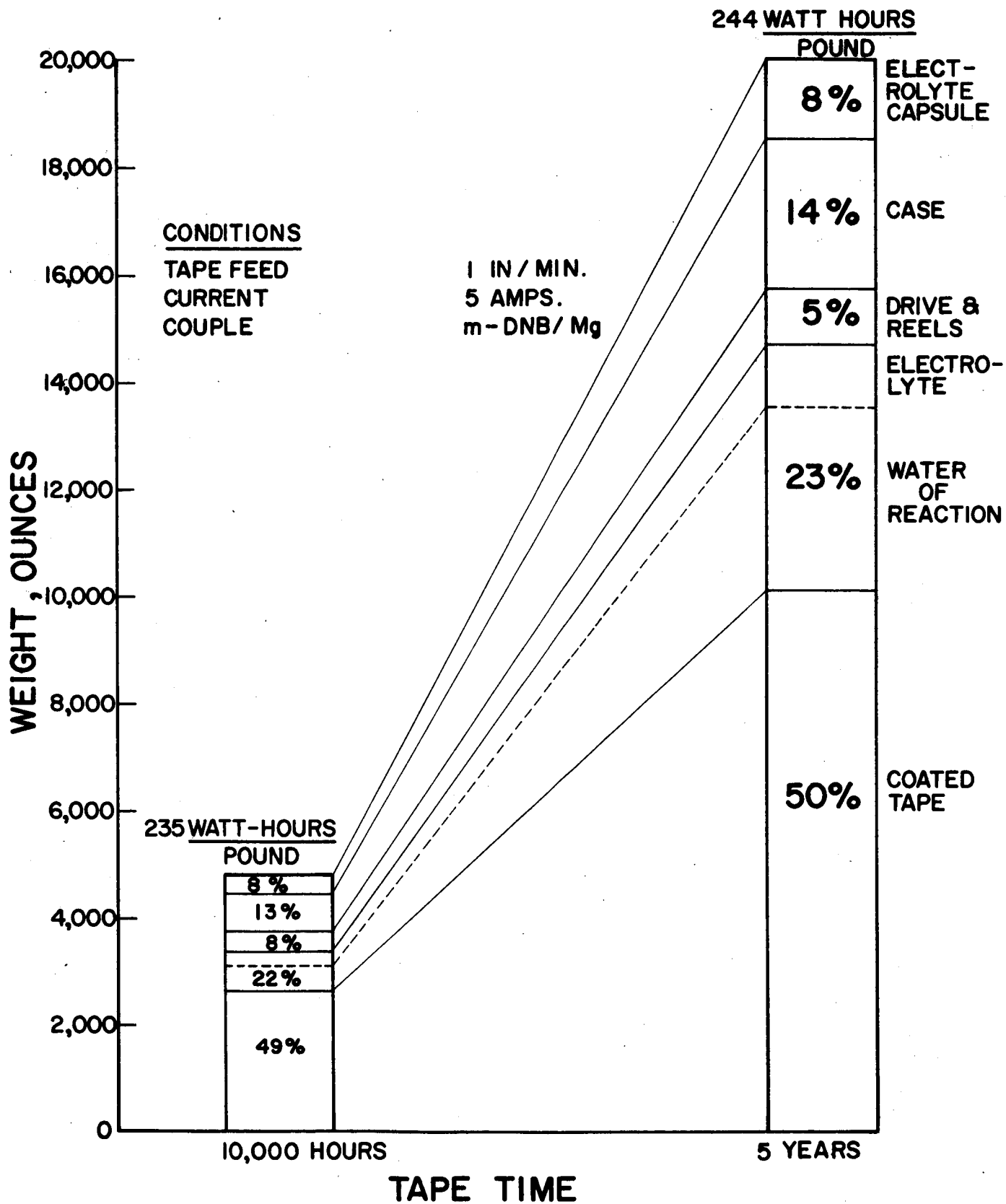Figure 19a.   Ultimate Tape System Advantages

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Figure 19b. Ultimate Tape System Advantages

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The same analysis is carried through in Fig. 19(b) for mission times
of 10,000 hours and 5 years. Here, the point of maximum return has
apparently been reached since the fractional weights of the active
components do not increase and there is only a corresponding token
rise in energy density.

2. High Energy Anode Development

To incorporate aluminum or magnesium into a tape anode,the following
three structural forms are considered possible: (1) solid, as in
foil form; (2) porous, as in pressed powders or molded electrodes,
and (3) high area solid, as obtained from flame sprayed metals.
Accordingly, steps were taken to obtain samples of each type for
performance testing under various current densities. The foil or
sheet stock was purchased directly from the metal manufacturers and,
in the case of Mg, included several alloys. The flame spraying was
accomplished by a local vendor on tape backing materials of several
different compositions. The porous powder types will be manufactured
in the laboratory using a punch and die arrangement designed for this
purpose. The latter is shown in Fig. 20.

The testing phase is scheduled to follow, and electrical apparatus and
Plexiglas ® blocks are being readied as required. The initial tests
will include measurement of the degree of polarization with increasing
current density and the effect of different electrolytes.

C. ELECTROLYTE INCAPSULATION

Various methods of electrolyte incapsulation are being considered to
supply electrolyte as needed for discharge of the tape battery in a
storable form compatible with stop-start operation. To achieve a high
payload of electrolyte, the container wall must be thin. The smaller
the capsule size, the thinner the capsule wall must be to provide the
same percentage payload and, consequently, the more impermeable the
wall material must be. For example, with a 5-micron capsule, for 50%
volume initial payload, the wall thickness must be less than 1 micron.
With an assumed requirement of a minimum payload of 60% after three
years storage, micro-size capsules are eliminated as a possibility with
the present state-of-the-art, at least for incapsulation of aqueous
phases. In fact, it appears that microcapsules will be promising only
if the anode material is at least partially used as an incapsulant.
In this way, a much greater capsule wall thickness could be used
without increasing the weight penalty.
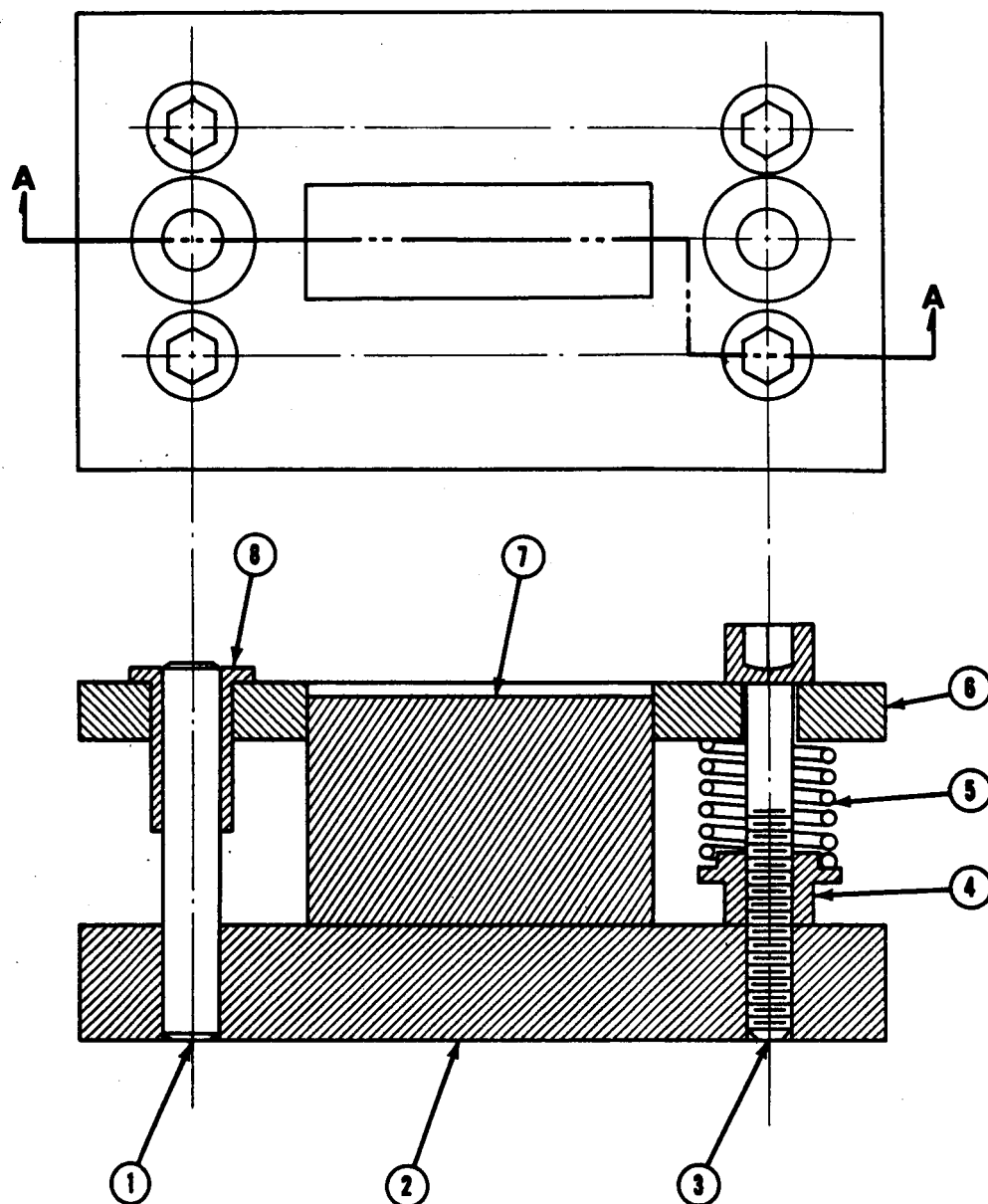
SECTION AA

LEGEND

1. Guide Pin
2. Base
3. Bolt
4. Locknut
5. Spring
6. ·Plate
7. Die
8. Bushing

Figure 20.   Die Mold for Porous Powder Electrode
             Manufacture

A very large macro-capsule can easily meet the above payload-storage requirements. For example, a 500-cc polyethylene bottle with 40- mm wall will provide a 95% + payload with a loss of only 1/4% per year. However, this means of electrolyte storage would require additional mechanisms to dispense electrolyte at the required rate to the desired location. Aside from the additional complexity, there is a definite minimum operation time below which this method suffers a weight penalty compared to micro-or-macro-capsules.

Our analysis indicates that for one set of assumed conditions, this minimum operation time is of the order of several hundred hours. While this minimum will vary with the conditions, a macro-incapsulation of dimensions suitable for supply with or on tape obviously offers the most promising approach. With this method, as with microcapsules, optimization is essentially independent of tape time and it appears possible to fulfill the payload and storage requirements; this is not so with microcapsules. The methods of incapsulation are illustrated along with a summary of the results of our paper analysis in terms of capsule weight versus tape time in Figure 21 . Microincapsulation appears to offer a weight advantage over macrocapsules as shown in Figure 21 for all periods of tape time. This is because loss of electrolyte payload is not taken into account. When loss of electrolyte due to capsule wall permeability is included, all three curves in Figure 21 will show a curvature upward, the rise being steepest for microincapsulation.

D. MULTIPLE CELL VOLTAGE

During the next phase of the development of a tape battery using high energy couples, operation at high voltage (multicell voltage) will be demonstrated. The following are three general approaches to providing a system with higher voltages, which have been, and will continue to be, considered:

(1) The first employs a voltage conversion device external to the electrochemical system. While this method remains a distinct possibility, it is felt that the necessary high conversion efficiency of such a device would require it to be designed around a constant load. It would presumably be operable under a varying load, but the efficiency would suffer.
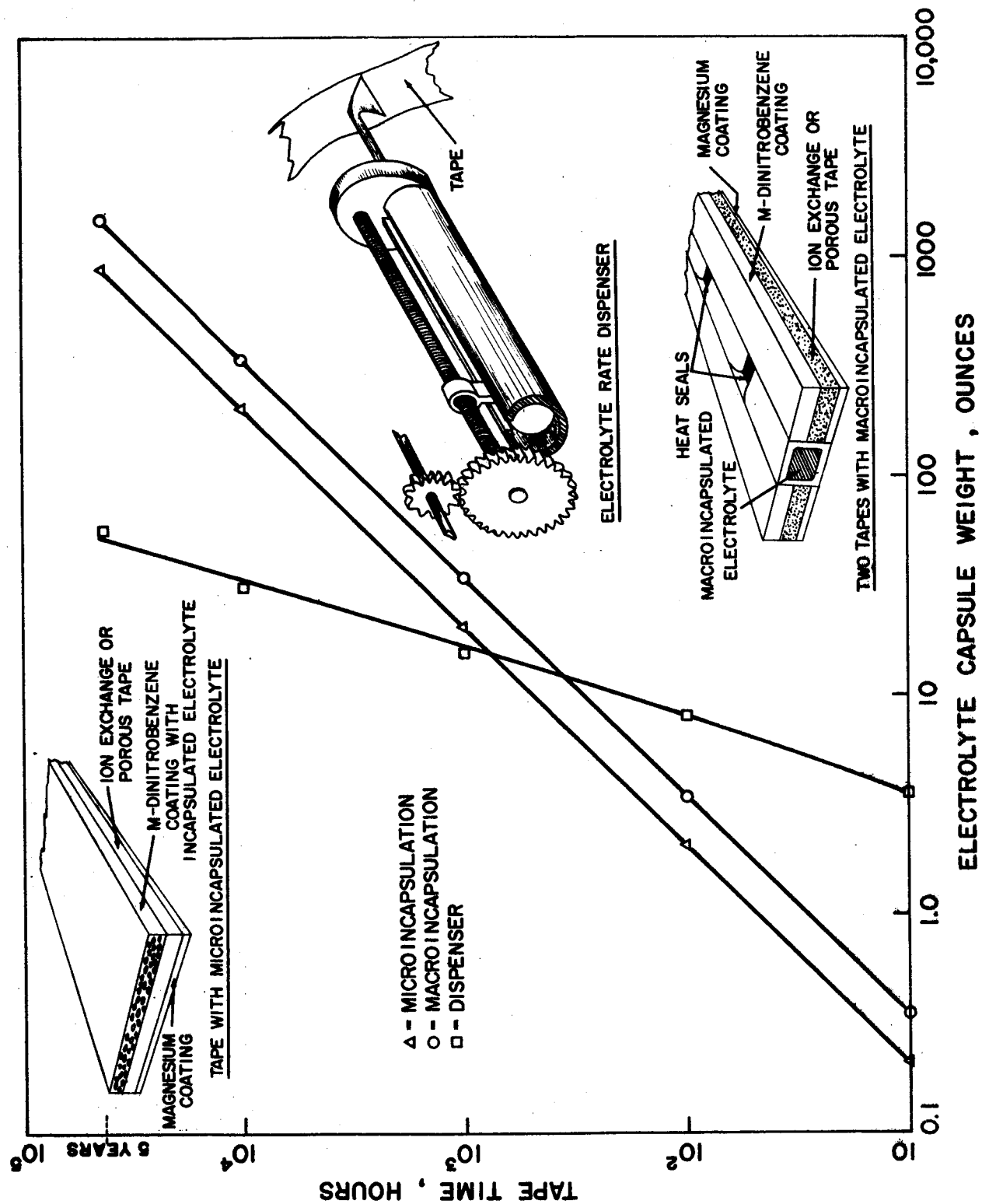
Figure 21. Electrolyte Container Weight vs Tape Time. Micro- and Macroincapsulation Methods

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(2)   The second method would be to use bi-polar or duplex
      electrodes. While this method offers unique advantages,
      its major application appeas to be for low current devices
      since any duplexing of tapes would necessarily increase the
      tape thickness and decrease its flexibility to such an extent
      that operation between the current collectors might suffer.
      For example, for a bi-polar tape system operating at 5 amperes and
      28 volts, the tape thickness would be approximately 1/4 inch.
      This would be a rather inflexible tape. However, there is the
      possibility of storing individual tapes on separate reels
      and duplexing them just before they enter the current collectors.

(3)   The third method of providing multiple cell voltages is perhaps
      the most obvious one: connecting individual tape deck modules
      in series. A schematic drawing of a single module is seen in
      Fig. 22 while a 4-cell stack is shown in Fig. 23. Each stack
      of cells would be powered by a parasitic electrical drive
      mounted on the end plate of the stack. In the next phase of
      the development work on the tape concept this stacking principle
      will be used for providing multiple cell voltages.

E. CONVERSION DEVICE DEVELOPMENT

During this period, all of the work relating to the mechanical
design of the conversion device covered the selection of the type
of electric drive to be used during the next phase of development.
In line with the objectives of attaining maximum watt-hours per
pound of weight, and having an electric drive capable of variable
speed operation, the following different types of electric drives
were studied:

1. A 12-VDC permanent magnet motor with gear train. Rheostat in
    armature circuit to vary speed.

2. A shunt-wound dc motor with gear train; Rheostat in field
    circuit to vary speed.

3. A 3-VDC, constant-speed, permanent magnet motor with gear train;
    a variable speed transmission to vary speed.

4. A stepping motor or solenoid with electronic pulser; electronic
    pulser designed to vary pulse interval to vary speed.

5. A solenoid-wound spring motor; an adjustable escapement mechanism
    to vary speed.

TAKE-UP REEL

CARRIER

LOADED REEL

TAPE DRIVE WHEEL
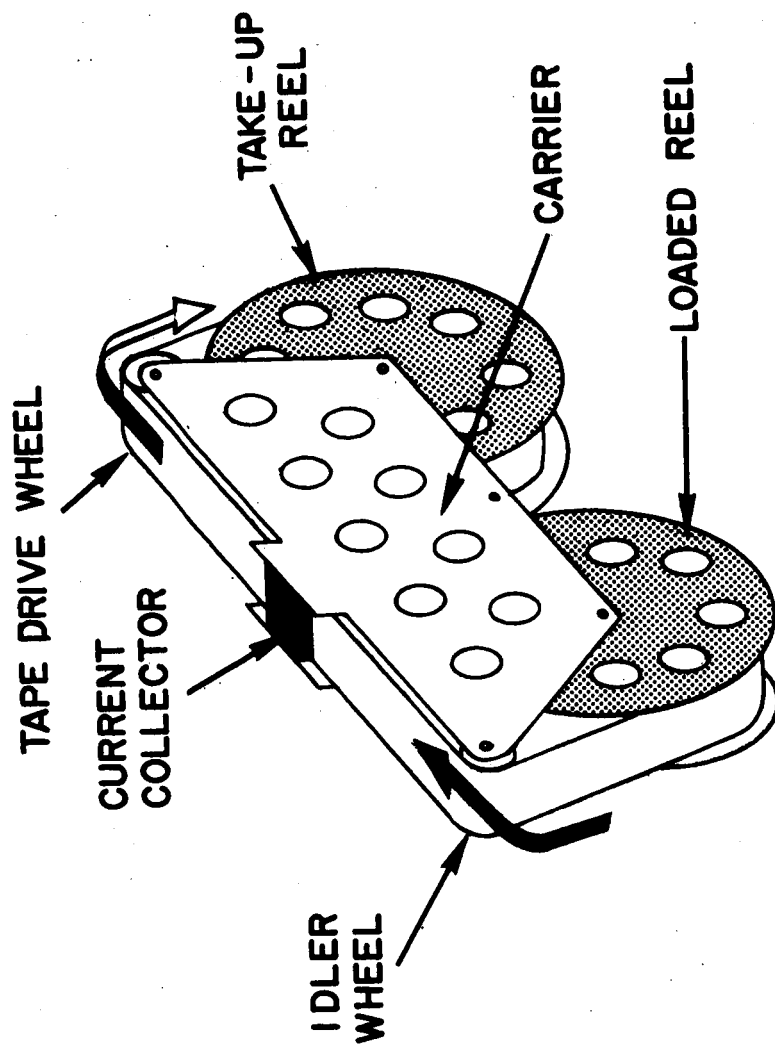
CURRENT COLLECTOR

IDLER WHEEL

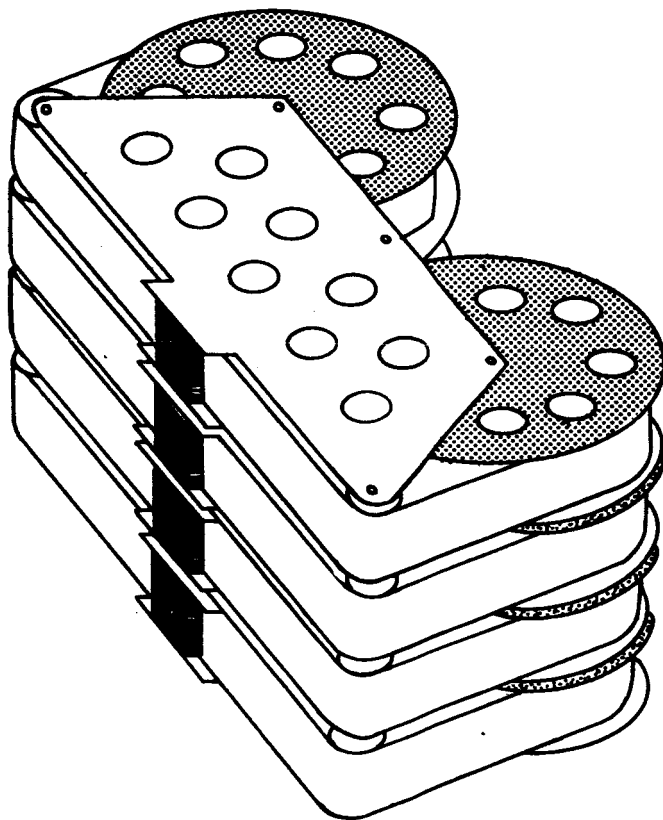Figure 22. Single Tape Deck Module

Figure 23. Stacked Tape Deck Modules

After evaluating various factors, the 3-VDC, constant speed motor with gear train and variable speed transmission was selected. The advantages of this type of drive for this application are as follows:

1. Operating voltage is low. Since the drive must operate parasitically from the voltage generated by the battery tape, low operating voltage will obviate the necessity of incorporating a DC voltage converter.

2. The output torque per pound of weight and per unit of power consumption is high.

3. The present state of the art in the design of lightweight, efficient, small, DC electric motors is very good, with advances being made continually.

4. A simple, lighweight, variable-speed transmission is feasible.

In the course of evaluating the above during this period, inquiries were sent to approximately 20 different companies who make small electric motors, in search of a small, lightweight, and efficient DC permanent magnet motor.

A motor with gear train capable of 30 to 40 ounce-inches at an output shaft speed of 1 rpm, requiring a input wattage of less than 0.20, and weighing less than 8 ounces was sought. Such a motor would be capable of driving approximately three tape cells.

After several weeks of search a motor with these requirements was offered by the Giavinini Controls Corporation. Accordingly, the following two motors were ordered:

	Motor No. 1	Motor No. 2
Design Voltage, VDC	3	12
Output Shaft Speed, rpm	1 rpm	1
Input, Milliwatts	0.21	0.21
Output Shaft Torque, oz-in.	30	30
Weight, oz.	8 1/2	8 1/2

The 12-VDC motor was ordered so that experiments could be conducted on a rheostat control of speed.

APPENDIX III

NEW TECHNOLOGY

The reportable items considered to have been developed during the term of the contract are as follows:

1. Silver peroxide/zinc tape cell using silver peroxide adhered to a tape base by a polyvinyl alcohol binder and a second tape carrying the KOH electrolyte, passed between an inert cathodic current collector and a consumable zinc anode during operation of the cell. This development is described in the present Final Report. It is considered an invention, and a patent application has been prepared and filed on this development: Bernard A. Gruber et al, SN 336,557, filed January 8, 1961, for Dry Tape Fuel Cell. This case has been reported to NASA with a Confirmatory License to the Government, and a request for waiver of patent title rights.

2. Tape cell with parasitic drive, electrolyte encapsulated for long-term storage, and tape carrying anode and cathode reaction components. This development is described in the present Final Report to the extent that work has been done up to the end of the contract period. It is considered novel technology, but determination of the patentable status of this work will have to await further progress of the development, scheduled to take place under a subsequent contract.